US009417542B2

(12) **United States Patent**
Hiroko et al.

(10) **Patent No.: US 9,417,542 B2**
(45) **Date of Patent: Aug. 16, 2016**

(54) **MAGNETIC TONER**

(71) Applicant: **CANON KABUSHIKI KAISHA**, Tokyo (JP)

(72) Inventors: **Shuichi Hiroko**, Tokyo (JP); **Michihisa Magome**, Mishima (JP); **Yusuke Hasegawa**, Suntou-gun (JP); **Yoshitaka Suzumura**, Mishima (JP)

(73) Assignee: **CANON KABUSHIKI KAISHA**, Tokyo (JP)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **14/364,065**

(22) PCT Filed: **Dec. 26, 2012**

(86) PCT No.: **PCT/JP2012/084286**

§ 371 (c)(1),
(2) Date: **Jun. 9, 2014**

(87) PCT Pub. No.: **WO2013/100182**

PCT Pub. Date: **Jul. 4, 2013**

(65) **Prior Publication Data**

US 2014/0370431 A1 Dec. 18, 2014

(30) **Foreign Application Priority Data**

Dec. 27, 2011 (JP) 2011-285912

(51) **Int. Cl.**
G03G 9/097 (2006.01)
G03G 9/083 (2006.01)
(Continued)

(52) **U.S. Cl.**
CPC ***G03G 9/0833*** (2013.01); ***G03G 9/0806*** (2013.01); ***G03G 9/08708*** (2013.01);
(Continued)

(58) **Field of Classification Search**
CPC G03G 9/0833; G03G 9/0806; G03G 9/08708; G03G 9/08711; G03G 9/09725; G03G 9/08795; G03G 9/08797; G03G 9/09708; G03G 9/08782
See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

5,066,558 A 11/1991 Hikake et al.
6,132,919 A 10/2000 Ogawa et al.
(Continued)

FOREIGN PATENT DOCUMENTS

CN 101061439 A 10/2007
JP 2-167561 * 6/1990 ..... G03G 9/08
(Continued)

OTHER PUBLICATIONS

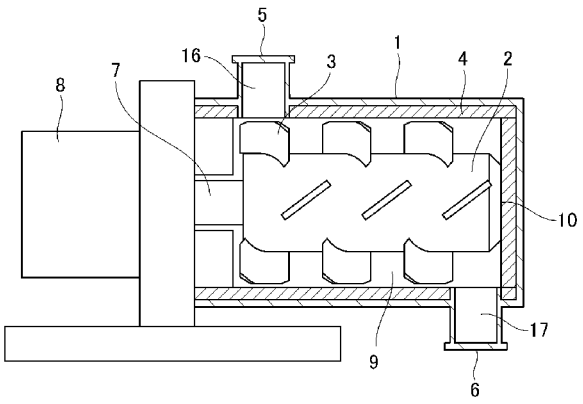
Translation of JP 2-167561 published Jun. 1990.*
(Continued)

Primary Examiner — Peter Vajda
(74) *Attorney, Agent, or Firm* — Fitzpatrick, Cella, Harper & Scinto

(57) **ABSTRACT**

A magnetic toner contains magnetic toner particles containing a binder resin, a release agent, and a magnetic body, and inorganic fine particles present on the surface of the magnetic toner particles, wherein a ratio of coverage of the magnetic toner particles' surface by the inorganic fine particles is in a prescribed range for the magnetic toner, the inorganic fine particles contain prescribed metal oxide fine particles, with at least 85 mass % of the metal oxide fine particles being silica fine particles, the coefficient of variation on the coverage ratio A is in a prescribed range, the binder resin contains a styrene resin, in a GPC measurement of a THF-soluble matter in the magnetic toner, a peak molecular weight (Mp) of a main peak is in a prescribed range, and a prescribed fatty acid ester compound is incorporated as a release agent.

2 Claims, 7 Drawing Sheets



(51) **Int. Cl.**
G03G 9/08 (2006.01)
G03G 9/087 (2006.01)

(52) **U.S. Cl.**
CPC ***G03G9/08711*** (2013.01); ***G03G 9/08782*** (2013.01); ***G03G 9/08795*** (2013.01); ***G03G 9/08797*** (2013.01); ***G03G 9/09708*** (2013.01); ***G03G 9/09725*** (2013.01)

(56) **References Cited**

U.S. PATENT DOCUMENTS

6,485,876	B1	11/2002	Takezawa et al.	
7,740,998	B2	6/2010	Yamazaki et al.	
2012/0045717	A1*	2/2012	Hiroko et al.	430/106.1

FOREIGN PATENT DOCUMENTS

JP	4-145448	A	5/1992
JP	10-48869	A	2/1998
JP	2001-117267	A	4/2001
JP	2001-272813	A	10/2001
JP	2003-57867	A	2/2003
JP	3812890	B2	8/2006
JP	2006-284728	A	10/2006
JP	3863289	B2	12/2006
JP	2007-264669	A	10/2007
JP	2007-293043	A	11/2007
JP	2008-15248	A	1/2008
JP	2010-79312	A	4/2010

OTHER PUBLICATIONS

U.S. Appl. No. 14/364,067, filed Jun. 9, 2014. Applicant: Hasegawa, et al.
U.S. Appl. No. 14/364,068, filed Jun. 9, 2014. Applicant: Magome, et al.
U.S. Appl. No. 14/362,380, filed Jun. 2, 2014. Applicant: Suzumura, et al.
U.S. Appl. No. 14/362,377, filed Jun. 2, 2014. Applicant: Matsui, et al.
U.S. Appl. No. 14/364,636, filed Jun. 11, 2014. Applicant: Sano, et al.
U.S. Appl. No. 14/364,634, filed Jun. 11, 2014. Applicant: Uratani, et al.
U.S. Appl. No. 14/364,640, filed Jun. 11, 2014. Applicant: Nomura, et al.
U.S. Appl. No. 14/364,638, filed Jun. 11, 2014. Applicant: Tanaka, et al.
U.S. Appl. No. 14/364,633, filed Jun. 11, 2014. Applicant: Ohmori, et al.
PCT International Search Report and Written Opinion of the International Searching Authority, International Application No. PCT/JP2012/084286, Mailing Date Feb. 12, 2013.
Taiwanese Office Action dated Jan. 16, 2015 in Taiwanese Application No. 101150557.

* cited by examiner

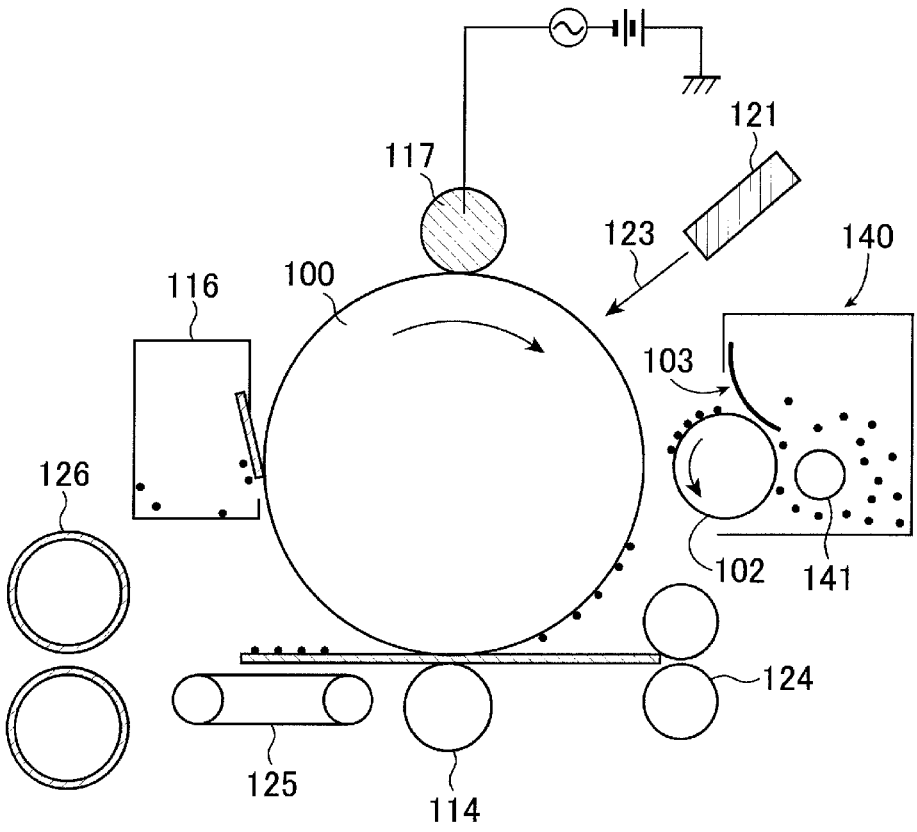


Fig. 1

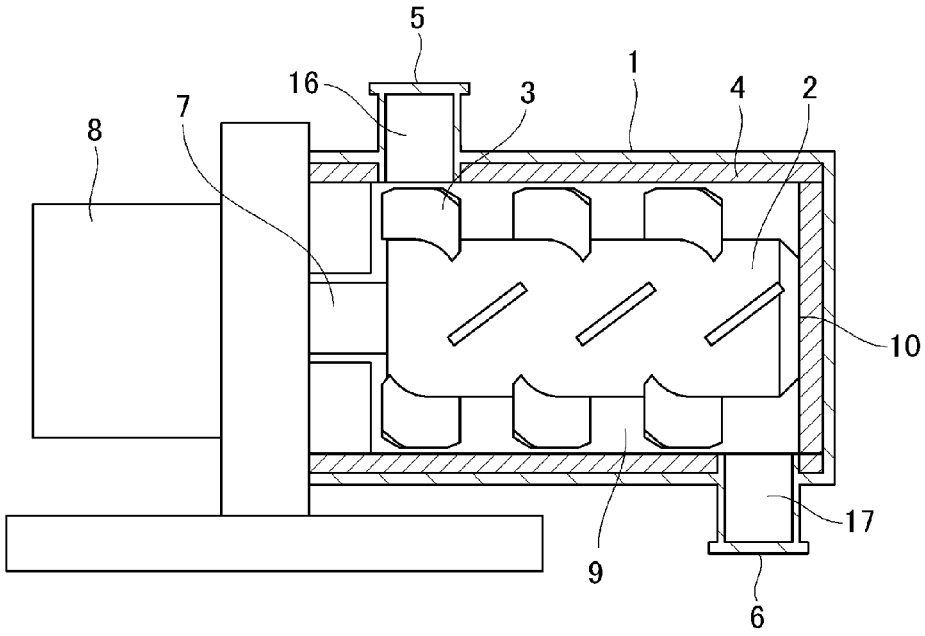


Fig. 2

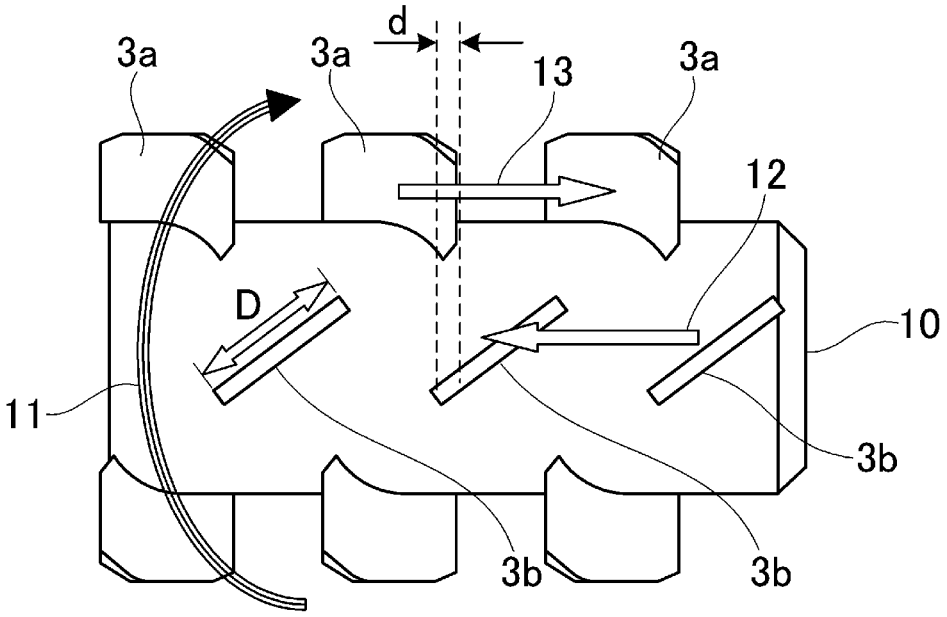


Fig. 3

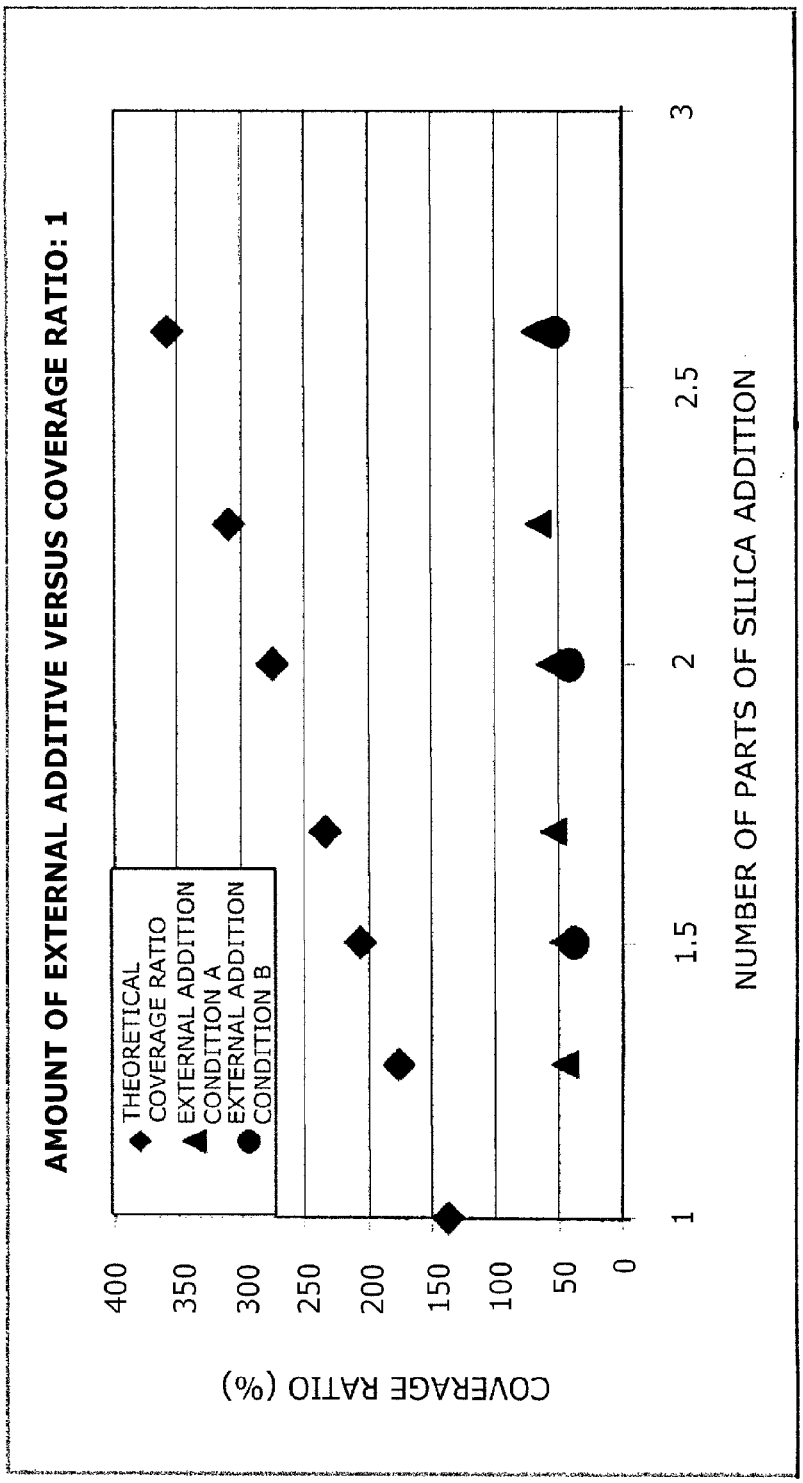

AMOUNT OF EXTERNAL ADDITIVE VERSUS COVERAGE RATIO: 1
THEORETICAL COVERAGE RATIO
EXTERNAL ADDITION CONDITION A
EXTERNAL ADDITION CONDITION B
COVERAGE RATIO (%)
400
350
300
250
200
150
100
50
0
1
1.5
2
2.5
3
NUMBER OF PARTS OF SILICA ADDITION

Fig. 4

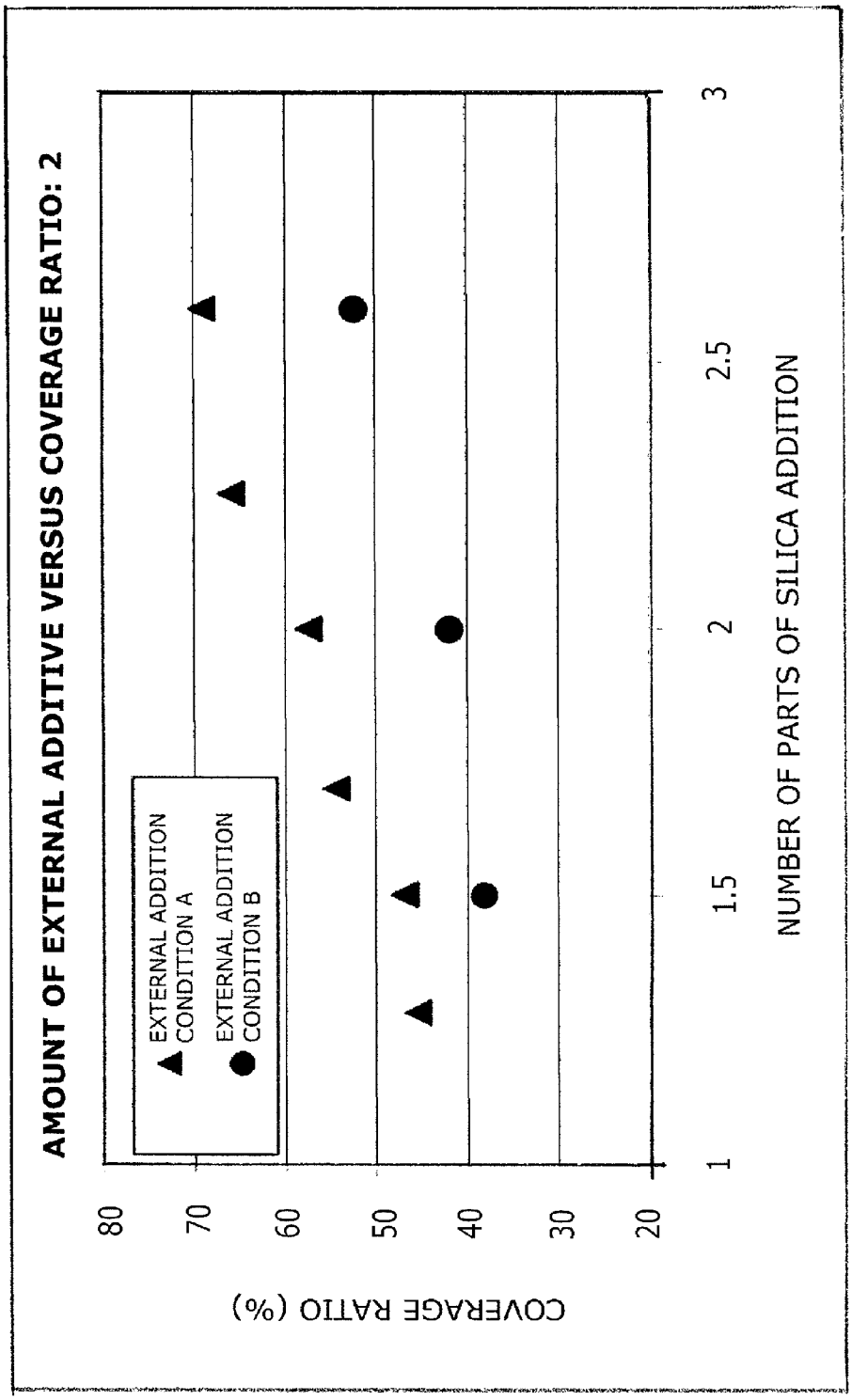

AMOUNT OF EXTERNAL ADDITIVE VERSUS COVERAGE RATIO: 2
EXTERNAL ADDITION CONDITION A
EXTERNAL ADDITION CONDITION B
COVERAGE RATIO (%)
80
70
60
50
40
30
20
1
1.5
2
2.5
3
NUMBER OF PARTS OF SILICA ADDITION

Fig. 5

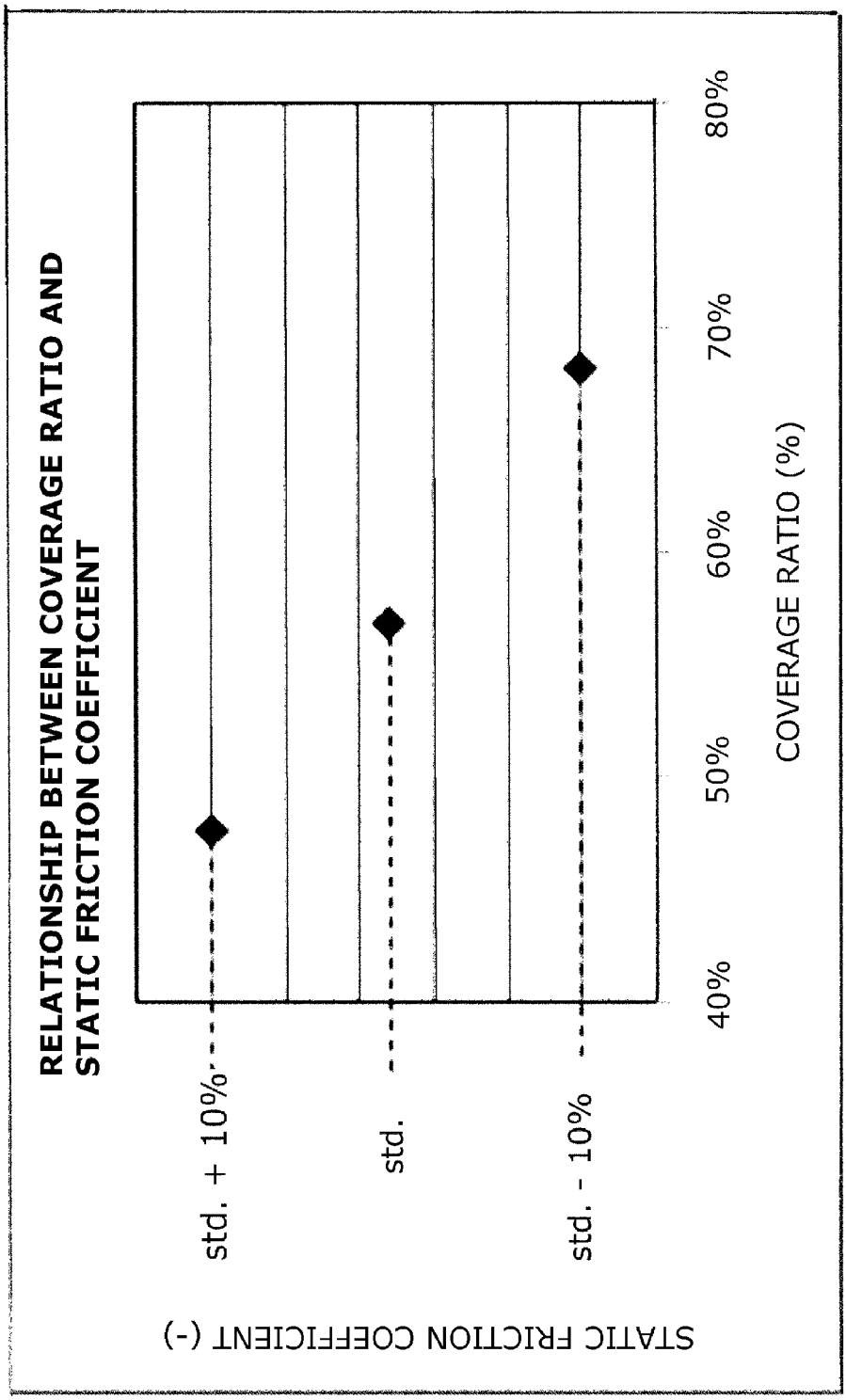

RELATIONSHIP BETWEEN COVERAGE RATIO AND STATIC FRICTION COEFFICIENT
STATIC FRICTION COEFFICIENT (-)
std. + 10%
std.
std. - 10%
40%
50%
60%
70%
80%
COVERAGE RATIO (%)

Fig. 6

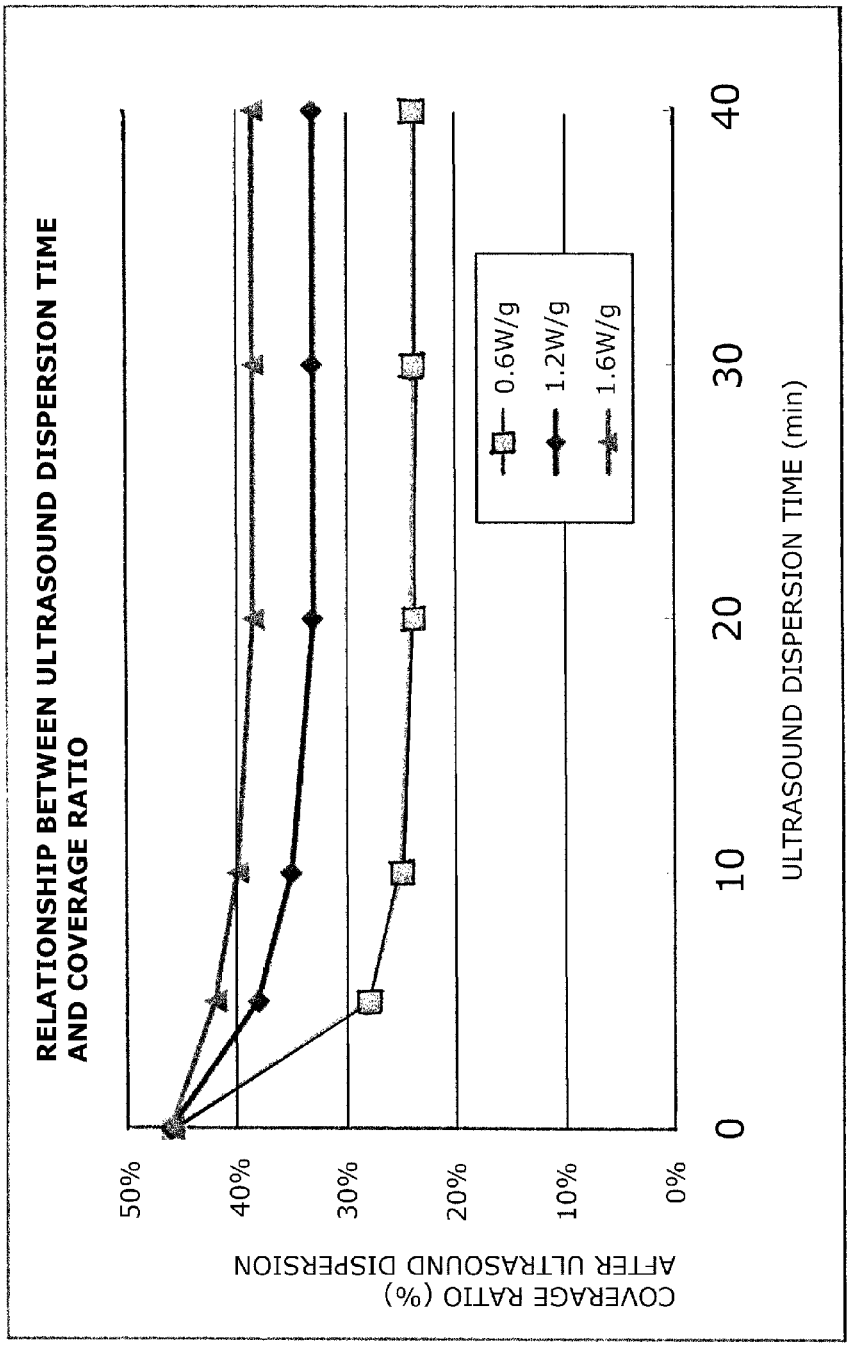

RELATIONSHIP BETWEEN ULTRASOUND DISPERSION TIME AND COVERAGE RATIO
COVERAGE RATIO (%) AFTER ULTRASOUND DISPERSION
50%
40%
30%
20%
10%
0%
0
10
20
30
40
ULTRASOUND DISPERSION TIME (min)
0.6W/g
1.2W/g
1.6W/g

Fig. 7

MAGNETIC TONER

TECHNICAL FIELD

The present invention relates to a magnetic toner for use in, for example, electrophotographic methods, electrostatic recording methods, and magnetic recording methods.

BACKGROUND ART

Image-forming apparatuses, e.g., copiers and printers, have in recent years been experiencing increasing diversification in their intended applications and use environments as well as demand for additional improvements in speed, image quality, and stability.

In addition, device downsizing and enhancements in energy efficiency are also occurring in copiers and printers at the same time, and magnetic monocomponent development systems that use a magnetic toner adapted to these trends are preferably used in this context.

In order for device downsizing and energy efficiency enhancements to coexist, it is essential to simplify not only the development structure, but to also simplify the fixing apparatus in the fixing structure. Simplification of the fixing apparatus can be achieved, for example, by using film fixing, which facilitates simplification of the heating source and the structure of the apparatus.

However, film fixing generally uses light pressures, and, when in particular the amount of heat is reduced with the goal of achieving an energy-saving fixing operation, an adequate amount of heat may not be obtained—depending on various factors such as the state of the surface of the media, e.g., the type of paper—and fixing defects may occur as a result.

When the goal is such a size reduction and energy conservation, an improved toner is desired that will enable a satisfactory fixing, regardless of the media, even in a light-pressure fixing step such as film fixing and that will thus enable the developing performance to coexist in balance with size reduction and energy conservation.

To respond to this problem, an improved low-temperature fixability and storability are pursued in Patent Literature 1 through the use of two release agents that exhibit different solubilities in the binder resin. However, room for improvement still remains here from the standpoint of the balance with image stability during durability testing.

An improvement in the offset resistance and fixing performance is pursued in Patent Literature 2 by controlling the state using an ester compound composed of a carboxylic acid and pentaerythritol or dipentaerythritol. However, room for improvement still remains here from the standpoint of the image stability during durability testing.

On the other hand, in order to solve the problems associated with external additives, toners have been disclosed with a particular focus on the release of external additives (refer to Patent Literatures 3 and 4). These have also not been satisfactory in terms of improving the low-temperature fixability of the toner.

Moreover, Patent Literature 5 teaches stabilization of the development • transfer steps by controlling the total coverage ratio of the toner base particles by the external additives, and a certain effect is in fact obtained by controlling the theoretical coverage ratio, provided by calculation, for a certain prescribed toner base particle. However, the actual state of binding by external additives may be substantially different from the value calculated assuming the toner to be a sphere, and, for magnetic toners in particular, achieving the effects of the present invention in terms of low-temperature fixability without controlling the actual state of external additive binding has proven to be entirely unsatisfactory.

CITATION LIST

Patent Literature

[PTL 1] Japanese Patent Application Publication No. 2003-057867
[PTL 2] Japanese Patent Publication No. 3863289
[PTL 3] Japanese Patent Application Publication No. 2001-117267
[PTL 4] Japanese Patent Publication No. 3812890
[PTL 4] Japanese Patent Application Publication No. 2007-293043

SUMMARY OF INVENTION

Technical Problems

An object of the present invention is to provide a magnetic toner that can solve the problems identified above.

Specially, an object of the present invention is to provide a magnetic toner that yields a stable image density regardless of the use environment and that can also exhibit desired low-temperature fixability.

The present inventors discovered that the problems can be solved by specifying the relationship between the coverage ratio of the magnetic toner particles' surface by the inorganic fine particles and the coverage ratio of the magnetic toner particles' surface by inorganic fine particles that are fixed to the magnetic toner particles' surface and by specifying the resin composition of the magnetic toner. The present invention was achieved based on this discovery.

Thus, the present invention is described as follows:

A magnetic toner comprising: magnetic toner particles comprising a binder resin, a release agent, and a magnetic body; and inorganic fine particles present on the surface of the magnetic toner particles, wherein

the inorganic fine particles present on the surface of the magnetic toner particles comprise metal oxide fine particles, the metal oxide fine particles containing silica fine particles, and optionally containing titania fine particles and alumina fine particles, and a content of the silica fine particles being at least 85 mass % with respect to a total mass of the silica fine particles, the titania fine particles and the alumina fine particles;

when a coverage ratio A(%) is a coverage ratio of the magnetic toner particles' surface by the inorganic fine particles and a coverage ratio B(%) is a coverage ratio of the magnetic toner particles' surface by the inorganic fine particles that are fixed to the magnetic toner particles' surface,

the magnetic toner has a coverage ratio A of at least 45.0% and not more than 70.0% and a coefficient of variation on the coverage ratio A of not more than 10.0%, and

a ratio [coverage ratio B/coverage ratio A] of the coverage ratio B to the coverage ratio A of at least 0.50 and not more than 0.85; wherein

the binder resin comprises a styrene resin and, in a measurement using gel permeation chromatography of the tetrahydrofuran-soluble matter in the magnetic toner, the peak molecular weight (Mp) of the main peak is from at least 4000 to not more than 8000; and wherein

the release agent comprises at least one of fatty acid ester compounds selected from the group consisting of a tetrafunctional fatty acid ester compound, a pentafunctional fatty acid ester compound and a hexafunctional fatty acid ester com-

pound, and the fatty acid ester compound has a melting point of from at least 60° C. to not more than 90° C.

Advantageous Effects of Invention

The present invention can provide a magnetic toner that, regardless of the use environment, yields a stable image density and can provide excellent low-temperature fixability.

BRIEF DESCRIPTION OF DRAWINGS

FIG. **1** is a schematic diagram that shows an example of an image-forming apparatus;

FIG. **2** is a schematic diagram that shows an example of a mixing process apparatus that can be used for the external addition and mixing of inorganic fine particles;

FIG. **3** is a schematic diagram that shows an example of the structure of a stirring member used in the mixing process apparatus;

FIG. **4** is a diagram that shows an example of the relationship between the number of parts of silica addition and the coverage ratio;

FIG. **5** is a diagram that shows an example of the relationship between the number of parts of silica addition and the coverage ratio;

FIG. **6** is a diagram that shows an example of the relationship between the coverage ratio and the static friction coefficient; and

FIG. **7** is a diagram that shows an example of the relationship between the ultrasound dispersion time and the coverage ratio.

DESCRIPTION OF EMBODIMENTS

The present invention is described in detail below.

The present invention relates to a magnetic toner comprising: magnetic toner particles containing a binder resin, a release agent, and a magnetic body; and inorganic fine particles present on the surface of the magnetic toner particles, wherein

the inorganic fine particles present on the surface of the magnetic toner particles contain metal oxide fine particles, the metal oxide fine particles containing silica fine particles, and optionally containing titania fine particles and alumina fine particles, and a content of the silica fine particles being at least 85 mass % with respect to a total mass of the silica fine particles, the titania fine particles and the alumina fine particles;

when a coverage ratio A(%) is a coverage ratio of the magnetic toner particles' surface by the inorganic fine particles and a coverage ratio B(%) is a coverage ratio of the magnetic toner particles' surface by the inorganic fine particles that are fixed to the magnetic toner particles' surface,

the magnetic toner has a coverage ratio A of at least 45.0% and not more than 70.0% and a coefficient of variation on the coverage ratio A of not more than 10.0%, and

a ratio [coverage ratio B/coverage ratio A] of the coverage ratio B to the coverage ratio A of at least 0.50 to not more than 0.85;

wherein the binder resin contains a styrene resin and, in a measurement using gel permeation chromatography of the tetrahydrofuran-soluble matter in the magnetic toner, the peak molecular weight (Mp) of the main peak is from at least 4000 to not more than 8000; and

wherein the release agent contains at least one of fatty acid ester compounds selected from the group consisting of a tetrafunctional fatty acid ester compound, a pentafunctional fatty acid ester compound and a hexafunctional fatty acid ester compound, and the fatty acid ester compound has a melting point of from at least 60° C. to not more than 90° C.

As a result of their investigations, the present inventors discovered that the use of the above-described magnetic toner makes it possible to obtain a stable image density regardless of the use environment and to substantially improve the low-temperature fixability.

The low-temperature fixability could be made to coexist in balance with the developing performance by setting the resin structure of the binder resin as described above and by setting the state of the external addition of the inorganic fine particles as described above. While the reasons for this are not entirely clear, the present inventors hypothesize as follows.

A large exudation by the release agent occurs with the above-described resin structure for the binder resin and the above-described state of external addition for the inorganic fine particles, and this increases the releasability by the magnetic toner versus a fixing member such as a fixing film. This presumably results in an enhanced fixing performance onto the paper.

The process of fixing a toner is a process in which adherence to the media, e.g., paper, is brought about by promoting melting and deformation of the toner by heat of the fixing member. Thus, when the amount of heat is lowered with the goal of achieving an energy-sparing fixing, it is crucial in order to achieve adherence by the toner on the media that the force inducing attachment onto the media be larger than the force inducing attachment to the fixing film.

By doing this, the heat can be efficiently conveyed to all the toner on the media and a satisfactory fixing performance can then be obtained even at low amounts of heat.

Thus, enhancing the releasability of the toner from the fixing member and bringing about a relative increase in the adherence of the toner to the paper is considered to be crucial to improving the fixing performance exhibited by the toner.

The magnetic toner of the present invention contains a styrene resin in the binder resin and, in a measurement using gel permeation chromatography (GPC) of the tetrahydrofuran (THF)-soluble matter in the magnetic toner, the peak molecular weight (Mp) of the main peak must be from at least 4000 to not more than 8000. In addition, the release agent in the magnetic toner of the present invention contains at least one of fatty acid ester compounds selected from the group consisting of a tetrafunctional fatty acid ester compound, a pentafunctional fatty acid ester compound and a hexafunctional fatty acid ester compound, and the fatty acid ester compound has a melting point of from at least 60° C. to not more than 90° C.

Establishing the resin structure described above causes the resin to have a substantial deformability and causes the release agent to have a substantial exudation behavior. It is believed that as a result the desired low-temperature fixability appears due to an increase in the releasability of the magnetic toner from the fixing member and an increase in the relative adhesiveness (anchoring effect) to the paper.

The heat-induced deformability of the magnetic toner is thought to be increased according to the present invention by controlling the peak molecular weight (Mp) of the main peak in GPC measurement of the THF-soluble matter in the magnetic toner to the relatively low molecular weight of from at least 4000 to not more than 8000.

In addition, it is thought that a state in which the release agent is easily melted by the heating during fixing and readily extruded to the toner surface can be set up in advance by the use of a release agent with a melting point of from at least 60° C. to not more than 90° C.

Moreover, the use of at least one of fatty acid ester compounds selected from the group consisting of a tetrafunctional fatty acid ester compound, a pentafunctional fatty acid ester compound and a hexafunctional fatty acid ester compound for the release agent is thought to promote the exudation of the release agent to the toner surface by increasing the bulkiness of the release agent itself and restraining the compatibility in the toner between the binder resin and the release agent.

This extensive control of the release agent and resin structure as described above is believed to promote the extrusion of the release agent to the toner surface and so provide a satisfactory releasability of the magnetic toner from the fixing member, e.g., a fixing film, and thereby substantially improve the adherence (anchoring effect) to the paper.

Moreover, letting the coverage ratio A(%) be the coverage ratio of the magnetic toner particles' surface by the inorganic fine particles and letting the coverage ratio B(%) be the coverage ratio of the magnetic toner particles' surface by the inorganic fine particles that are fixed to the magnetic toner particles' surface, it is critical for the magnetic toner of the present invention that the coverage ratio A be at least 45.0% and not more than 70.0% and that the ratio [coverage ratio B/coverage ratio A, also referred to below simply as B/A] of the coverage ratio B to the coverage ratio A be at least 0.50 and not more than 0.85.

By having the coverage ratio A and B/A—which represent the state of external addition of the inorganic fine particles—satisfy the prescribed ranges in a toner that has a high release performance as described above, it becomes possible for the first time for a desired low-temperature fixability and a desired developing performance to coexist in balance.

While the reasons for this are not entirely clear, the following reasons are believed to apply. After the transfer step, the toner on the paper is adhered and fixed on the paper by passage through the fixing unit. In the stage prior to fixing, a state is present in which transfer has occurred from the photosensitive member onto the media, for example, paper, and as a consequence mobility is still possible in this state. Increasing the area of contact by the fixing unit with the toner on the paper after this transfer step, i.e., increasing the toner population that directly contacts the fixing member as much as possible, is thought to be effective for achieving a uniform and unskewed transfer of heat from the fixing unit to the toner with maximum efficiency. A uniform toner layer on the paper—particularly controlling to a condition in which the surface contacting the fixing unit is as free of unevenness as possible—is thought to be effective as a consequence.

Since the coverage ratio A has a high value of from at least 45.0% to not more than 70.0% in the magnetic toner of the present invention, the van der Waals forces and electrostatic forces with the contact members are low and the toner-to-toner adhesiveness is also low. Due to this, after the transfer step the toner resists aggregation due to this low toner-to-toner adhesiveness and the toner layer is more closely packed. As a consequence, the toner layer is made more uniform and the presence of unevenness in the upper region of the toner layer is inhibited and the area contacting the fixing unit is enlarged.

As a result, the range of usable media, e.g., paper, can also be broadened. For example, even in a circumstance in which the paper itself is very uneven, e.g., as with rough paper, and the toner layer is prone to be made nonuniform, a suitable uniformization is achieved due to the low toner-to-toner adhesiveness and the same results can be obtained as for smooth paper.

In addition, due to the low van der Waals force and electrostatic force with the fixing member, e.g., a fixing film, exercised by the magnetic toner of the present invention, a high releasability from the fixing member is obtained and a relative promotion of the anchoring effect to the paper can be brought about.

The low van der Waals force and low electrostatic force are considered in the following. First, with regard to the van der Waals force, the van der Waals force (F) produced between a flat plate and a particle is represented by the following equation.

$$F=H\times D/(12Z^2)$$

Here, H is Hamaker's constant, D is the diameter of the particle, and Z is the distance between the particle and the flat plate. With respect to Z, it is generally held that an attractive force operates at large distances and a repulsive force operates at very small distances, and Z is treated as a constant since it is unrelated to the state of the magnetic toner particle surface. According to the preceding equation, the van der Waals force (F) is proportional to the diameter of the particle in contact with the flat plate. When this is applied to the magnetic toner surface, the van der Waals force (F) is smaller for an inorganic fine particle, with its smaller particle size, in contact with the flat plate than for a magnetic toner particle in contact with the flat plate. That is, the van der Waals force is smaller for the case of contact through the intermediary of the inorganic fine particles provided as an external additive than for the case of direct contact between the magnetic toner particle and the fixing member.

Furthermore, the electrostatic force can be regarded as a reflection force. It is known that a reflection force generally is directly proportional to the square of the particle charge (q) and inversely proportional to the square of the distance.

In the case of the charging of a magnetic toner, it is the surface of the magnetic toner particle and not the inorganic fine particles that bears the charge. Due to this, the reflection force declines as the distance between the surface of the magnetic toner particle and the flat plate (here, the fixing member) grows larger.

That is, when, in the case of the magnetic toner surface, the magnetic toner particle comes into contact with the flat plate through the intermediary of the inorganic fine particles, a distance is set up between the flat plate and the surface of the magnetic toner particle and the reflection force is lowered as a result.

As described in the preceding, the van der Waals force and reflection force produced between the magnetic toner and the fixing member are reduced by having inorganic fine particles be present at the magnetic toner particle surface and having the magnetic toner come into contact with the fixing member with the inorganic fine particles interposed therebetween. That is, the attachment force between the magnetic toner and the fixing member is reduced.

Whether the magnetic toner particle directly contacts the fixing member or is in contact therewith through the intermediary of the inorganic fine particles, depends on the amount of inorganic fine particles coating the magnetic toner particle surface, i.e., on the coverage ratio by the inorganic fine particles.

It is thought that the opportunity for direct contact between the magnetic toner particles and the fixing member is diminished at a high coverage ratio by the inorganic fine particles, which makes it more difficult for the magnetic toner to stick to the fixing member.

As has been noted above, it is thought that the attachment force to a member can be reduced by raising the coverage ratio by the inorganic fine particles. Tests were therefore

carried out on the attachment force with a member and the coverage ratio by the inorganic fine particles.

The relationship between the coverage ratio for the magnetic toner and the attachment force with a member was indirectly inferred by measuring the static friction coefficient between an aluminum substrate and spherical polystyrene particles having different coverage ratios by silica fine particles.

Specifically, the relationship between the coverage ratio and the static friction coefficient was determined using spherical polystyrene particles (weight-average particle diameter (D**4**)=7.5 μm) that had different coverage ratios (coverage ratio determined by SEM observation) by silica fine particles.

More specifically, spherical polystyrene particles to which silica fine particles had been added were pressed onto an aluminum substrate. The substrate was moved to the left and right while changing the pressing pressure, and the static friction coefficient was calculated from the resulting stress. This was performed for the spherical polystyrene particles at each different coverage ratio, and the obtained relationship between the coverage ratio and the static friction coefficient is shown in FIG. **6**.

The static friction coefficient determined by the preceding technique is thought to correlate with the sum of the van der Waals and reflection forces acting between the spherical polystyrene particles and the substrate. As may be understood from the graph, a higher coverage ratio by the silica fine particles results in a lower static coefficient of friction. It may be inferred from this that a magnetic toner having a high coverage rate also has a low attachment force for a member.

The inorganic fine particles must be added in large amounts in order to bring the coverage ratio A above 70.0%, but, even if an external addition method could be devised here, image defects (vertical streaks) brought about by released inorganic fine particles are then readily produced and this is therefore disfavored.

This coverage ratio A, coverage ratio B, and ratio [B/A] of the coverage ratio B to the coverage ratio A can be determined by the methods described below.

The coverage ratio A used in the present invention is a coverage ratio that also includes the easily-releasable inorganic fine particles, while the coverage ratio B is the coverage ratio due to inorganic fine particles that are fixed to the magnetic toner particle surface and are not released in the release process described below. It is thought that the inorganic fine particles represented by the coverage ratio B are fixed in a semi-embedded state in the magnetic toner particle surface and therefore do not undergo displacement even when the magnetic toner is subjected to shear on the developing sleeve or on the electrostatic latent image-bearing member.

The inorganic fine particles represented by the coverage ratio A, on the other hand, include the fixed inorganic fine particles described above as well as inorganic fine particles that are present in the upper layer and have a relatively high degree of freedom.

As noted above, it is thought that the inorganic fine particles that can be present between magnetic toner particles and between the magnetic toner and the various members participate in bringing about the effect of diminished van der Waals forces and diminished electrostatic forces and that having a high coverage ratio A is particularly critical with regard to this effect.

As noted above, deformability by the resin and exudation by the release agent are crucial for improving the low-temperature fixability of the magnetic toner. The present inventors discovered that the low-temperature fixability of the magnetic toner could be very substantially improved by establishing a high coverage ratio A.

That B/A is at least 0.50 to not more than 0.85 means that inorganic fine particles fixed to the magnetic toner surface are present to a certain degree and that in addition inorganic fine particles in a readily releasable state (a state that enables behavior separated from the magnetic toner particle) are also present thereon in a favorable amount. It is thought that a bearing-like effect is generated presumably by the releasable inorganic fine particles sliding against the fixed inorganic fine particles and that the aggregative forces between the magnetic toners are then substantially reduced.

According to the results of investigations by the present inventors, it was found that this bearing effect and the above-described attachment force-reducing effect are maximally obtained when both the fixed inorganic fine particles and the easily releasable inorganic fine particles are relatively small inorganic fine particles having a primary particle number-average particle diameter (D**1**) of approximately not more than 50 nm. Accordingly, the coverage ratios A and B were calculated focusing on the inorganic fine particles having a diameter of not more than 50 nm.

By setting prescribed ranges for the coverage ratio A and B/A for the magnetic toner of the present invention, the attachment force between the magnetic toner and various members can be reduced and the aggregative forces between the magnetic toners can be substantially diminished. As a result, because the magnetic toner layer is uniformized through a closest packing of the magnetic toner, the area of contact between the toner and the fixing film can be increased during passage through the fixing unit. In addition, through the combination with the exudation performance of the release agent brought about by an optimization of the structures of the binder resin and release agent, for the first time a very efficient anchoring effect to the media can be obtained and the desired fixing performance can be exhibited. Due to this, the production of toner for which the thermal conduction is inadequate can be substantially reduced even in the case of structures where a reduction in the thermal transfer efficiency is prone to occur, such as in particular in the combination of rough paper with fixing at light pressures using a fixing film.

It is important that the coefficient of variation on the coverage ratio A is not more than 10.0% in the present invention. The coefficient of variation is more preferably not more than 8.0%. The coefficient of variation on the coverage ratio A of not more than 10.0% means that the coverage ratio A is very uniform between magnetic toner particles and within magnetic toner particle. When the coefficient of variation exceeds 10.0%, the state of coverage of the magnetic toner surface is nonuniform, which impairs the ability to lower the aggregative forces between the magnetic toners.

There are no particular limitations on the technique for bringing the coefficient of variation to 10.0% or below, but it is preferable that adjustment is implemented in use of the external addition apparatus and technique described below, which are capable of bringing about a high degree of spreading of the metal oxide fine particles, e.g., silica fine particles, over the magnetic toner particles' surface.

With regard to the coverage ratio by the inorganic fine particles used as an external additive, this can be derived—making the assumption that the inorganic fine particles and the magnetic toner have a spherical shape—using the equation described, for example, in Patent Literature 5. However, there are also many instances in which the inorganic fine particles and/or the magnetic toner do not have a spherical shape, and in addition the inorganic fine particles may also be present in an aggregated state on the magnetic toner particle

surface. As a consequence, the coverage ratio derived using the indicated technique does not pertain to the present invention.

The present inventors therefore carried out observation of the magnetic toner surface with the scanning electron microscope (SEM) and determined the coverage ratio for the actual coverage of the magnetic toner particle surface by the inorganic fine particles.

As one example, the theoretical coverage ratio and the actual coverage ratio were determined for mixtures prepared by adding different amounts of silica fine particles (number of parts of silica addition per 100 mass parts of magnetic toner particles) to magnetic toner particles (magnetic body content=43.5 mass %) provided by a pulverization method and having a volume-average particle diameter (Dv) of 8.0 μm (refer to FIGS. **4** and **5**). Silica fine particles with a volume-average particle diameter (Dv) of 15 nm were used for the silica fine particles. For the calculation of the theoretical coverage ratio, 2.2 g/cm^3 was used for the true specific gravity of the silica fine particles; 1.65 g/cm^3 was used for the true specific gravity of the magnetic toner; and monodisperse particles with a particle diameter of 15 nm and 8.0 μm were assumed for, respectively, the silica fine particles and the magnetic toner particles.

As is clear from the graph in FIG. **4**, the theoretical coverage ratio exceeds 100% as the number of parts of silica addition is increased. On the other hand, the coverage ratio obtained by actual observation does vary with the number of parts of silica addition, but does not exceed 100%. This is due to silica fine particles being present to some degree as aggregates on the magnetic toner surface or is due to a large effect from the silica fine particles not being spherical.

Moreover, according to investigations by the present inventors, it was found that, even at the same amount of addition by the silica fine particles, the coverage ratio varied with the external addition technique. That is, it is not possible to determine the coverage ratio uniquely from the amount of addition of the inorganic fine particles (refer to FIG. **5**). Here, external addition condition A refers to mixing at 1.0 W/g for a processing time of 5 minutes using the apparatus shown in FIG. **2**. External addition condition B refers to mixing at 4000 rpm for a processing time of 2 minutes using an FM10C Henschel mixer (from Mitsui Miike Chemical Engineering Machinery Co., Ltd.).

For the reasons provided in the preceding, the present inventors used the inorganic fine particle coverage ratio obtained by SEM observation of the magnetic toner surface.

For the present invention, the binder resin in the magnetic toner comprises a styrene resin. While the reason for this is not entirely clear, it is hypothesized that, because the ester group is not present as a main component in the principal skeleton of the binder resin, the at least tetrafunctional to not more than hexafunctional fatty acid ester compound used in the present invention is then able to easily engage in domain formation, thereby promoting the extrusion effect when fixing is carried out. This "domain formation" referenced by the present invention refers to the fatty acid ester compound being present in a phase-separated state in the binder resin.

The peak molecular weight (Mp) of the main peak when the tetrahydrofuran (THF)-soluble matter of this binder resin is submitted to measurement using gel permeation chromatography (GPC) is preferably from at least 4000 to not more than 8000. This Mp can be controlled into the indicated range by the judicious selection of the type of monomer forming the styrene resin, infra, and by suitable adjustment of the amount of the polymerization initiator.

The Mp of the binder resin is more preferably from at least 5000 to not more than 7000.

Specific examples of styrene resin include polystyrene and styrene copolymers such as styrene-propylene copolymers, styrene-vinyltoluene copolymers, styrene-methyl acrylate copolymers, styrene-ethyl acrylate copolymers, styrene-butyl acrylate copolymers, styrene-octyl acrylate copolymers, styrene-methyl methacrylate copolymers, styrene-ethyl methacrylate copolymers, styrene-butyl methacrylate copolymers, styrene-octyl methacrylate copolymers, styrene-butadiene copolymers, styrene-isoprene copolymers, styrene-maleic acid copolymers, and styrene-maleate copolymers. A single one of these may be used or a plurality may be used in combination.

The monomer used to form the aforementioned styrene resin can be exemplified by the following: styrene; styrene derivatives such as o-methylstyrene, m-methylstyrene, p-methylstyrene, p-methoxystyrene, p-phenylstyrene, p-chlorostyrene, 3,4-dichlorostyrene, p-ethylstyrene, 2,4-dimethylstyrene, p-n-butylstyrene, p-tert-butylstyrene, p-n-hexylstyrene, p-n-octylstyrene, p-n-nonylstyrene, p-n-decylstyrene, and p-n-dodecylstyrene; unsaturated monoolefins such as ethylene, propylene, butylene, and isobutylene; unsaturated polyenes such as butadiene and isoprene; vinyl halides such as vinyl chloride, vinylidene chloride, vinyl bromide, and vinyl fluoride; vinyl esters such as vinyl acetate, vinyl propionate, and vinyl benzoate; α-methylene aliphatic monocarboxylic acid esters such as methyl methacrylate, ethyl methacrylate, propyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, n-octyl methacrylate, dodecyl methacrylate, 2-ethylhexyl methacrylate, stearyl methacrylate, phenyl methacrylate, dimethylaminoethyl methacrylate, and diethylaminoethyl methacrylate; acrylates such as methyl acrylate, ethyl acrylate, n-butyl acrylate, isobutyl acrylate, propyl acrylate, n-octyl acrylate, dodecyl acrylate, 2-ethylhexyl acrylate, stearyl acrylate, 2-chloroethyl acrylate, and phenyl acrylate; vinyl ethers such as vinyl methyl ether, vinyl ethyl ether, and vinyl isobutyl ether; vinyl ketones such as vinyl methyl ketone, vinyl hexyl ketone, and methyl isopropenyl ketone; N-vinyl compounds such as N-vinylpyrrole, N-vinylcarbazole, N-vinylindole, and N-vinylpyrrolidone; vinylnaphthalenes; and derivatives of acrylic acid and methacrylic acid, such as acrylonitrile, methacrylonitrile, and acrylamide.

Additional examples are unsaturated dibasic acids such as maleic acid, citraconic acid, itaconic acid, alkenylsuccinic acid, fumaric acid, and mesaconic acid; unsaturated dibasic acid anhydrides such as maleic anhydride, citraconic anhydride, itaconic anhydride, and alkenylsuccinic anhydride; the half esters of unsaturated dibasic acids, such as the methyl half ester of maleic acid, ethyl half ester of maleic acid, butyl half ester of maleic acid, methyl half ester of citraconic acid, ethyl half ester of citraconic acid, butyl half ester of citraconic acid, methyl half ester of itaconic acid, methyl half ester of alkenylsuccinic acid, methyl half ester of fumaric acid, and methyl half ester of mesaconic acid; unsaturated dibasic acid esters such as dimethyl maleate and dimethyl fumarate; α,β-unsaturated acids such as acrylic acid, methacrylic acid, crotonic acid, and cinnamic acid; α,β-unsaturated acid anhydrides such as crotonic anhydride and cinnamic anhydride, as well as the anhydrides of lower fatty acids with α,β-unsaturated acids; and monomers that contain the carboxyl group, such as alkenylmalonic acid, alkenylglutaric acid, and alkenyladipic acid and their acid anhydrides and monoesters.

Additional examples are acrylate esters and methacrylate esters, such as 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, and 2-hydroxypropyl methacrylate, and mono-

mers that contain the hydroxy group, such as 4-(1-hydroxy-1-methylbutyl)styrene and 4-(1-hydroxy-1-methylhexyl)styrene.

The styrene resin used in the binder resin in the magnetic toner of the present invention may have a crosslinked structure as provided by crosslinking with a crosslinking agent that contains two or more vinyl groups. The crosslinking agent used here can be exemplified by the following: aromatic divinyl compounds such as divinylbenzene and divinylnaphthalene;

diacrylate compounds in which linkage is effected by an alkyl chain, such as ethylene glycol diacrylate, 1,3-butylene glycol diacrylate, 1,4-butanediol diacrylate, 1,5-pentanediol diacrylate, 1,6-hexanediol diacrylate, neopentyl glycol diacrylate, and compounds provided by replacing the acrylate in the preceding compounds with methacrylate;

diacrylate compounds in which linkage is effected by an ether linkage-containing alkyl chain, such as diethylene glycol diacrylate, triethylene glycol diacrylate, tetraethylene glycol diacrylate, polyethylene glycol #400 diacrylate, polyethylene glycol #600 diacrylate, dipropylene glycol diacrylate, and compounds provided by replacing the acrylate in the preceding compounds with methacrylate;

diacrylate compounds in which linkage is effected by a chain containing an aromatic group and an ether linkage, such as polyoxyethylene(2)-2,2-bis(4-hydroxyphenyl)propane diacrylate, polyoxyethylene(4)-2,2-bis(4-hydroxyphenyl) propane diacrylate, and compounds provided by replacing the acrylate in the preceding compounds with methacrylate;

polyester-type diacrylate compounds, for example, MANDA (product name, Nippon Kayaku Co., Ltd.);

multifunctional crosslinking agents such as pentaerythritol triacrylate, trimethylolethane triacrylate, trimethylolpropane triacrylate, tetramethylolmethane tetraacrylate, oligoester acrylate, and compounds provided by replacing the acrylate in the preceding compounds with methacrylate, as well as triallyl cyanurate and triallyl trimellitate.

The crosslinking agent is used, expressed per 100 mass parts of the other monomer component, preferably at from 0.01 to 10 mass parts and more preferably at from 0.03 to 5 mass parts.

Among these crosslinking monomers, aromatic divinyl compounds (particularly divinylbenzene) and diacrylate compounds in which linkage is effected by a chain containing an aromatic group and an ether linkage are crosslinking monomers preferred for use in the binder resin from the standpoint of the fixing performance and offset resistance.

The polymerization initiator used in the production of the styrene resin can be exemplified by 2,2'-azobisisobutyronitrile, 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile), 2,2'-azobis(2,4-dimethylvaleronitrile), 2,2'-azobis(2-methylbutyronitrile), dimethyl 2,2'-azobisisobutyrate, 1,1'-azobis(1-cyclohexanecarbonitrile), 2-(carbamoylazo)isobutyronitrile, 2,2'-azobis(2,4,4-trimethylpentane), 2-phenylazo-2,4-dimethyl-4-methoxyvaleronitrile, 2,2-azobis(2-methylpropane), ketone peroxides (e.g., methyl ethyl ketone peroxide, acetylacetone peroxide, and cyclohexanone peroxide), 2,2-bis(t-butylperoxy)butane, t-butyl hydroperoxide, cumene hydroperoxide, 1,1,3,3-tetramethylbutyl hydroperoxide, di-t-butyl peroxide, t-butyl cumyl peroxide, dicumyl peroxide, α,α'-bis (t-butylperoxyisopropyl)benzene, isobutyl peroxide, octanoyl peroxide, decanoyl peroxide, lauroyl peroxide, 3,5,5-trimethylhexanoyl peroxide, benzoyl peroxide, m-toluoyl peroxide, diisopropyl peroxydicarbonate, di-2-ethylhexyl peroxydicarbonate, di-n-propyl peroxydicarbonate, di-2-ethoxyethyl peroxycarbonate, dimethoxyisopropyl peroxydicarbonate, di(3-methyl-3-methoxybutyl) peroxycarbonate, acetylcyclohexylsulfonyl peroxide, t-butyl peroxyacetate, t-butyl peroxyisobutyrate, t-butyl peroxyneodecanoate, t-butyl peroxy-2-ethylhexanoate, t-butyl peroxylaurate, t-butyl peroxybenzoate, t-butylperoxy isopropyl carbonate, di-t-butyl peroxyisophthalate, t-butylperoxy allyl carbonate, t-amyl peroxy-2-ethylhexanoate, di-t-butyl peroxyhexahydroterephthalate, and di-t-butyl peroxyazelate.

The magnetic body present in the magnetic toner in the present invention can be exemplified by iron oxides such as magnetite, maghemite, ferrite, and so forth; metals such as iron, cobalt, and nickel; and alloys and mixtures of these metals with metals such as aluminum, copper, magnesium, tin, zinc, beryllium, calcium, manganese, selenium, titanium, tungsten, and vanadium.

The number-average particle diameter (D1) of the primary particles of this magnetic body is preferably not more than 0.50 μm and more preferably is from 0.05 μm to 0.30 μm.

This magnetic body preferably has the following magnetic properties for the magnetic field application of 795.8 kA/m: a coercive force (H_c) preferably from 1.6 to 12.0 kA/m; a intensity of magnetization (σ_s) preferably from 50 to 200 Am^2/kg and more preferably from 50 to 100 Am^2/kg; and a residual magnetization (σ_r) preferably from 2 to 20 Am^2/kg.

The magnetic toner of the present invention preferably contains from at least 35 mass % to not more than 50 mass % of the magnetic body and more preferably contains from at least 40 mass % to not more than 50 mass %. If the magnetic toner contains the magnetic body in accordance with the abovementioned range, proper magnetic attraction exerted with a magnet roll in the developing sleeve can be obtained.

The content of the magnetic body in the magnetic toner can be measured using a Q5000IR TGA thermal analyzer from PerkinElmer Inc. With regard to the measurement method, the magnetic toner is heated from normal temperature to 900° C. under a nitrogen atmosphere at a rate of temperature rise of 25° C./minute: the mass loss from 100 to 750° C. is taken to be the component provided by subtracting the magnetic body from the magnetic toner and the residual mass is taken to be the amount of the magnetic body.

A charge control agent is preferably added to the magnetic toner of the present invention. The magnetic toner of the present invention is preferably a negative-charging toner.

Organometal complex compounds and chelate compounds are effective as charging agents for negative charging and can be exemplified by monoazo-metal complex compounds; acetylacetone-metal complex compounds; and metal complex compounds of aromatic hydroxycarboxylic acids and aromatic dicarboxylic acids.

Specific examples of commercially available products are Spilon Black TRH, T-77, and T-95 (Hodogaya Chemical Co., Ltd.) and BONTRON (registered trademark) S-34, S-44, S-54, E-84, E-88, and E-89 (Orient Chemical Industries Co., Ltd.).

A single one of these charge control agents may be used or two or more may be used in combination. Considered from the standpoint of the amount of charging of the magnetic toner, these charge control agents are used, expressed per 100 mass parts of the binder resin, preferably at from 0.1 to 10.0 mass parts and more preferably at from 0.1 to 5.0 mass parts.

Considered in terms of the ease of domain formation in the toner and the magnitude of the releasability, it is crucial that the release agent present in the magnetic toner of the present invention contains from the at least tetrafunctional to not more than hexafunctional fatty acid ester compound (i.e. tetrafunctional fatty acid ester compound, pentafunctional fatty acid ester compound, and hexafunctional fatty acid ester compound). The presence of a tetrafunctional fatty acid ester

compound is more preferred. The reason for this is that the release agent is then not too bulky and a more significant effect is obtained in terms of exudation to the toner surface. As has been noted above, exudation to the toner surface is believed to be promoted by increasing the bulkiness of the release agent itself and inhibiting its compatibility with the binder resin.

It is also crucial that the melting point of the release agent at the same time be from at least 60° C. to not more than 90° C.

It is thought here that the release agent itself then undergoes thorough melting when heat is applied during fixing, causing transition to a state in which extrusion to the toner surface easily occurs and causing a more effective promotion of its exudation.

The melting point of the release agent can be adjusted in the present invention by, for example, a judicious selection of the fatty acid and alcohol constituting the incorporated fatty acid ester.

The aforementioned fatty acid ester compound preferably comprises an ester compound of a fatty acid having from at least 18 to not more than 22 carbon atoms and an alcohol having from at least 4 to not more than 6 hydroxyl groups.

This is thought to be effective, when considering the above-described exudation to the toner surface, for the formation of domains by the release agent in the toner.

The bulkiness of the release agent itself must be adjusted in order for domain formation to occur, and the number of carbons in the fatty acid constituting the at least tetrafunctional to not more than hexafunctional fatty acid ester compound is therefore preferably in the range from at least 18 to not more than 22. Control into this range is preferred in order to further inhibit compatibility with the toner during toner fixing and provide a large exudation to the toner surface.

Pentaerythritol and dipentaerythritol are preferred for the alcohol component of the at least tetrafunctional to not more than hexafunctional fatty acid ester compound, while the number of carbons for the fatty acid is preferably from at least 18 to not more than 22.

The C_{18-22} fatty acid can be specifically exemplified by stearic acid, oleic acid, vaccenic acid, linoleic acid, linolenic acid, eleostearic acid, tuberculostearic acid, arachidic acid, arachidonic acid, and behenic acid. Saturated fatty acids are preferred among the preceding.

The release agent used in the present invention may also contain a wax in addition to the at least tetrafunctional to not more than hexafunctional fatty acid ester compound that has a melting point of from at least 60° C. to not more than 90° C.

This can provide additional promotion of the above-described deformability of the magnetic toner during fixing and a more substantial exudation behavior by the fatty acid ester compound.

This wax can be exemplified by the oxides of aliphatic hydrocarbon waxes, such as oxidized polyethylene wax, and their block copolymers; waxes in which the main component is an fatty acid ester, such as carnauba wax, sasol wax, and montanic acid ester waxes; and waxes provided by the partial or complete deacidification of fatty acid esters, such as deacidified carnauba wax. Additional examples are as follows: saturated straight-chain fatty acids such as palmitic acid, stearic acid, and montanic acid; unsaturated fatty acids such as brassidic acid, eleostearic acid, and parinaric acid; saturated alcohols such as stearyl alcohol, aralkyl alcohols, behenyl alcohol, carnaubyl alcohol, ceryl alcohol, and melissyl alcohol; long-chain alkyl alcohols; polyhydric alcohols such as sorbitol; fatty acid amides such as linoleamide, oleamide, and lauramide; saturated fatty acid bisamides such as methylenebisstearamide, ethylenebiscapramide, ethylenebislauramide, and hexamethylenebisstearamide; unsaturated fatty acid amides such as ethylenebisoleamide, hexamethylenebisoleamide, N,N'-dioleyladipamide, and N,N-dioleylsebacamide; aromatic bisamides such as m-xylenebisstearamide and N,N-distearylisophthalamide; fatty acid metal salts (generally known as metal soaps) such as calcium stearate, calcium laurate, zinc stearate, and magnesium stearate; waxes provided by grafting on an aliphatic hydrocarbon wax using a vinyl monomer such as styrene or acrylic acid; partial esters between a polyhydric alcohol and a fatty acid, such as behenic monoglyceride; and hydroxyl-containing methyl ester compounds obtained by the hydrogenation of plant oils.

The "melting point" of the fatty acid ester compound and the wax is measured based on ASTM D 3418-82 using a "DSC-7" (PerkinElmer Inc.) differential scanning calorimeter (DSC measurement instrument). The melting points of indium and zinc are used for temperature correction in the instrument's detection section, and the heat of fusion of indium is used to correct the amount of heat.

Specifically, 10 mg of the sample is accurately weighed out and placed in an aluminum pan and the measurement is carried out at a rate of temperature rise of 10° C./min in the measurement temperature range of 30 to 200° C. using an empty aluminum pan for reference. The measurement is performed by raising the temperature to 200° C. at 10° C./min, then lowering the temperature to 30° C. at 10° C./min, and thereafter raising the temperature once again at 10° C./min. The peak temperature of the maximum endothermic peak appearing in the DSC curve in the 30 to 200° C. temperature range in this second temperature ramp-up step is determined. This peak temperature of the maximum endothermic peak is taken to be the melting point of the fatty acid ester compound or wax.

The content of the release agent in the magnetic toner of the present invention, expressed per 100 mass parts of the binder resin, is preferably from 0.1 to 20 mass parts and more preferably from 0.5 to 10 mass parts.

In addition, when a wax is used in the present invention along with the at least tetrafunctional to not more than hexafunctional fatty acid ester compound having a melting point of from at least 60° C. to 90° C., the proportion of the at least tetrafunctional to not more than hexafunctional fatty acid ester compound having a melting point of from at least 60° C. to 90° C. with respect to the total release agent content is preferably from at least 20 mass % to not more than 80 mass % from the standpoint of being able to establish an even better coexistence between the fixing performance and developing performance.

These release agents can be incorporated in the binder resin, for example, by a method in which, during binder resin production, the binder resin is dissolved in a solvent, the temperature of the binder resin solution is raised, and addition and mixing are carried out while stirring, or a method in which addition is performed during melt kneading during toner production.

The magnetic toner of the present invention contains inorganic fine particles at the magnetic toner particles' surface.

The inorganic fine particles present on the magnetic toner particles' surface can be exemplified by silica fine particles, titania fine particles, and alumina fine particles, and these inorganic fine particles can also be favorably used after the execution of a hydrophobic treatment on the surface thereof.

It is critical that the inorganic fine particles present on the surface of the magnetic toner particles in the present invention contain at least one of metal oxide fine particle selected from the group consisting of silica fine particles, titania fine par-

ticles, and alumina fine particles, and that at least 85 mass % of the metal oxide fine particles be silica fine particles. Preferably at least 90 mass % of the metal oxide fine particles are silica fine particles. The reasons for this are that silica fine particles not only provide the best balance with regard to imparting charging performance and flowability, but are also excellent from the standpoint of lowering the aggregative forces within the toner.

The reason why silica fine particles are excellent from the standpoint of lowering the aggregative forces between the toners are not entirely clear, but it is hypothesized that this is probably due to the substantial operation of the previously described bearing effect with regard to the sliding behavior between the silica fine particles.

In addition, silica fine particles are preferably the main component of the inorganic fine particles fixed to the magnetic toner particle surface. Specifically, the inorganic fine particles fixed to the magnetic toner particle surface preferably contain at least one of metal oxide fine particle selected from the group consisting of silica fine particles, titania fine particles, and alumina fine particles wherein silica fine particles are at least 80 mass % of these metal oxide fine particles. The silica fine particles are more preferably at least 90 mass %. This is hypothesized to be for the same reasons as discussed above: silica fine particles are the best from the standpoint of imparting charging performance and flowability, and as a consequence a rapid initial rise in magnetic toner charge occurs. The result is that a high image density can be obtained, which is strongly preferred.

Here, adjustment is implemented on the basis of the timing and amount of addition of the inorganic fine particles in order to bring the silica fine particles to at least 85 mass % of the metal oxide fine particles present on the magnetic toner particle surface and in order to also bring the silica fine particles to at least 80 mass % with reference to the metal oxide particles fixed on the magnetic toner particle surface.

The amount of inorganic fine particles present can be checked using the methods described below for quantitating the inorganic fine particles.

<Quantitation Methods for the Inorganic Fine Particles>

(1) Determination of the Content of Silica Fine Particles in the Magnetic Toner (Standard Addition Method)

3 g of the magnetic toner is introduced into an aluminum ring having a diameter of 30 mm and a pellet is prepared using a pressure of 10 tons. The silicon (Si) intensity is determined (Si intensity-1) by wavelength-dispersive x-ray fluorescence analysis (XRF). The measurement conditions are preferably optimized for the XRF instrument used and all of the intensity measurements in a series are performed using the same conditions.

Separately, silica fine particles with a primary particle number-average particle diameter of 12 nm are added to the magnetic toner at 1.0 mass % with reference to the magnetic toner and mixing is carried out with a coffee mill. For the silica fine particles admixed at this time, silica fine particles with a primary particle number-average particle diameter of from at least 5 nm to not more than 50 nm can be used without affecting this determination.

After mixing, pellet fabrication is carried out as described above and the Si intensity (Si intensity-2) is determined also as described above. Using the same procedure, the Si intensity (Si intensity-3, Si intensity-4) is also determined for samples prepared by adding and mixing the silica fine particles at 2.0 mass % and 3.0 mass % of the silica fine particles with reference to the magnetic toner. The silica content (mass %) in the magnetic toner based on the standard addition method is calculated using Si intensities-1 to -4.

The titania content (mass %) in the magnetic toner and the alumina content (mass %) in the magnetic toner are determined using the standard addition method and the same procedure as described above for the determination of the silica content. That is, for the titania content (mass %), titania fine particles with a primary particle number-average particle diameter of from at least 5 nm to not more than 50 nm are added and mixed and the determination can be made by determining the titanium (Ti) intensity. For the alumina content (mass %), alumina fine particles with a primary particle number-average particle diameter of from at least 5 nm to not more than 50 nm are added and mixed and the determination can be made by determining the aluminum (Al) intensity.

(2) Separation of the Inorganic Fine Particles from the Magnetic Toner Particles

5 g of the magnetic toner is weighed using a precision balance into a lidded 200-mL plastic cup; 100 mL methanol is added; and dispersion is carried out for 5 minutes using an ultrasound disperser. The magnetic toner is held using a neodymium magnet and the supernatant is discarded. The process of dispersing with methanol and discarding the supernatant is carried out three times, followed by the addition of 100 mL of 10% NaOH and several drops of "Contaminon N" (a 10 mass % aqueous solution of a neutral pH 7 detergent for cleaning precision measurement instrumentation and comprising a nonionic surfactant, an anionic surfactant, and an organic builder, from Wako Pure Chemical Industries, Ltd.), light mixing, and then standing at quiescence for 24 hours. This is followed by re-separation using a neodymium magnet. Repeated washing with distilled water is carried out at this point until NaOH does not remain. The recovered particles are thoroughly dried using a vacuum drier to obtain particles A. The externally added silica fine particles are dissolved and removed by this process. Titania fine particles and alumina fine particles can remain present in particles A since they are sparingly soluble in 10% NaOH.

(3) Measurement of the Si Intensity in the Particles A

3 g of the particles A are introduced into an aluminum ring with a diameter of 30 mm; a pellet is fabricated using a pressure of 10 tons; and the Si intensity (Si intensity-5) is determined by wavelength-dispersive XRF. The silica content (mass %) in particles A is calculated using the Si intensity-5 and the Si intensities-1 to -4 used in the determination of the silica content in the magnetic toner.

(4) Separation of the Magnetic Body from the Magnetic Toner

100 mL of tetrahydrofuran is added to 5 g of the particles A with thorough mixing followed by ultrasound dispersion for 10 minutes. The magnetic body is held with a magnet and the supernatant is discarded. This process is performed 5 times to obtain particles B. This process can almost completely remove the organic component, e.g., resins, outside the magnetic body. However, because tetrahydrofuran-insoluble matter in the resin can remain, the particles B provided by this process are preferably heated to 800° C. in order to burn off the residual organic component, and the particles C obtained after heating are approximately the magnetic body that was present in the magnetic toner.

Measurement of the mass of the particles C yields the magnetic body content W (mass %) in the magnetic toner. In order to correct for the increment due to oxidation of the magnetic body, the mass of particles C is multiplied by 0.9666 ($Fe_2O_3 \rightarrow Fe_3O_4$).

(5) Measurement of the Ti Intensity and al Intensity in the Separated Magnetic Body

Ti and Al may be present as impurities or additives in the magnetic body. The amount of Ti and Al attributable to the

magnetic body can be detected by FP quantitation in wavelength-dispersive XRF. The detected amounts of Ti and Al are converted to titania and alumina and the titania content and alumina content in the magnetic body are then calculated.

The amount of externally added silica fine particles, the amount of externally added titania fine particles, and the amount of externally added alumina fine particles are calculated by substituting the quantitative values obtained by the preceding procedures into the following formulas.

amount of externally added silica fine particles (mass %)=silica content (mass %) in the magnetic toner−silica content (mass %) in particle A

amount of externally added titania fine particles (mass %)=titania content (mass %) in the magnetic toner−{titania content (mass %) in the magnetic body×magnetic body content W/100}

amount of externally added alumina fine particles (mass %)=alumina content (mass %) in the magnetic toner−{alumina content (mass %) in the magnetic body×magnetic body content W/100}

(6) Calculation of the Proportion of Silica Fine Particles in the Metal Oxide Fine Particles Selected from the Group Consisting of Silica Fine Particles, Titania Fine Particles, and Alumina Fine Particles, for the Inorganic Fine Particles Fixed to the Magnetic Toner Particle Surface

After carrying out the procedure, "Removing the unfixed inorganic fine particles", in the method described below for calculating the coverage ratio B and thereafter drying the toner, the proportion of the silica fine particles in the metal oxide fine particles can be calculated by carrying out the same procedures as in the method of (1) to (5) described above.

The number-average particle diameter (D1) of the primary particles in the inorganic fine particles in the present invention is preferably from at least 5 nm to not more than 50 nm and more preferably is from at least 10 nm to not more than 35 nm. Bringing the number-average particle diameter (D1) of the primary particles in the inorganic fine particles into the indicated range facilitates favorable control of the coverage ratio A and B/A and facilitates the generation of the above-described bearing effect and attachment force-reducing effect. When the primary particle number-average particle diameter (D1) is less than 5 nm, the inorganic fine particles are prone to aggregate with one another and not only it is then difficult to obtain large values for B/A, but the coefficient of variation on the coverage ratio A also readily assumes large values. When, on the other hand, the primary particle number-average particle diameter (D1) is larger than 50 nm, the coverage ratio A is then prone to be low even for large amounts of addition of the inorganic fine particles, while the value of B/A also tends to be low because the inorganic fine particles are difficult to fix to the magnetic toner particles. More specifically, when the primary particle number-average particle diameter (D1) is greater than 50 nm, the abovementioned reduction in adhesiveness and bearing effect cannot be obtained easily.

A hydrophobic treatment is preferably carried out on the inorganic fine particles used in the present invention, and particularly preferred inorganic fine particles will have been hydrophobically treated to a hydrophobicity, as measured by the methanol titration test, of at least 40% and more preferably at least 50%.

The method for carrying out the hydrophobic treatment can be exemplified by methods in which treatment is carried out with, e.g., an organosilicon compound, a silicone oil, a long-chain fatty acid, and so forth.

The organosilicon compound can be exemplified by hexamethyldisilazane, trimethylsilane, trimethylethoxysilane, isobutyltrimethoxysilane, trimethylchlorosilane, dimethyldichlorosilane, methyltrichlorosilane, dimethylethoxysilane, dimethyldimethoxysilane, diphenyldiethoxysilane, and hexamethyldisiloxane. A single one of these can be used or a mixture of two or more can be used.

The silicone oil can be exemplified by dimethylsilicone oil, methylphenylsilicone oil, a-methylstyrene-modified silicone oil, chlorophenyl silicone oil, and fluorine-modified silicone oil.

A C_{10-22} fatty acid is suitably used for the long-chain fatty acid, and the long-chain fatty acid may be a straight-chain fatty acid or a branched fatty acid. A saturated fatty acid or an unsaturated fatty acid may be used.

Among the preceding, C_{10-22} straight-chain saturated fatty acids are highly preferred because they readily provide a uniform treatment of the surface of the inorganic fine particles.

These straight-chain saturated fatty acids can be exemplified by capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, arachidic acid, and behenic acid.

Inorganic fine particles that have been treated with silicone oil are preferred for the inorganic fine particles used in the present invention, and inorganic fine particles treated with an organosilicon compound and a silicone oil are more preferred. This makes possible a favorable control of the hydrophobicity.

The method for treating the inorganic fine particles with a silicone oil can be exemplified by a method in which the silicone oil is directly mixed, using a mixer such as a Henschel mixer, with inorganic fine particles that have been treated with an organosilicon compound, and by a method in which the silicone oil is sprayed on the inorganic fine particles. Another example is a method in which the silicone oil is dissolved or dispersed in a suitable solvent; the inorganic fine particles are then added and mixed; and the solvent is removed.

In order to obtain a good hydrophobicity, the amount of silicone oil used for the treatment, expressed per 100 mass parts of the inorganic fine particles, is preferably from at least 1 mass parts to not more than 40 mass parts and is more preferably from at least 3 mass parts to not more than 35 mass parts.

In order to impart an excellent flowability to the magnetic toner, the silica fine particles, titania fine particles, and alumina fine particles used by the present invention have a specific surface area as measured by the BET method based on nitrogen adsorption (BET specific surface area) preferably of from at least 20 m^2/g to not more than 350 m^2/g and more preferably of from at least 25 m^2/g to not more than 300 m^2/g.

Measurement of the specific surface area (BET specific surface area) by the BET method based on nitrogen adsorption is performed based on JIS Z8830 (2001). A "TriStar300 (Shimadzu Corporation) automatic specific surface area ● pore distribution analyzer", which uses gas adsorption by a constant volume technique as its measurement procedure, is used as the measurement instrument.

The amount of addition of the inorganic fine particles, expressed per 100 mass parts of the magnetic toner particles, is preferably from at least 1.5 mass parts to not more than 3.0 mass parts of the inorganic fine particles, more preferably from at least 1.5 mass parts to not more than 2.6 mass parts, and even more preferably from at least 1.8 mass parts to not more than 2.6 mass parts.

Setting the amount of addition of the inorganic fine particles in the indicated range is also preferred from the stand-

point of facilitating appropriate control of the coverage ratio A and B/A and also from the standpoint of the image density and fogging.

Exceeding 3.0 mass parts for the amount of addition of the inorganic fine particles, even if an external addition apparatus and an external addition method could be devised, gives rise to release of the inorganic fine particles and facilitates the appearance of, for example, a streak on the image.

In addition to the above-described inorganic fine particles, particles with a primary particle number-average particle diameter (D**1**) of from at least 80 nm to not more than 3 μm may be added to the magnetic toner of the present invention. For example, a lubricant, e.g., a fluororesin powder, zinc stearate powder, or polyvinylidene fluoride powder; a polish, e.g., a cerium oxide powder, a silicon carbide powder, or a strontium titanate powder; or a spacer particle such as silica, may also be added in small amounts that do not influence the effects of the present invention.

Viewed from the standpoint of the balance between the developing performance and the fixing performance, the weight-average particle diameter (D**4**) of the magnetic toner of the present invention is preferably from at least 6.0 μm to not more than 10.0 μm and more preferably is from at least 7.0 μm to not more than 9.0 μm.

In addition, viewed from the standpoint of suppressing charge up, the average circularity of the magnetic toner of the present invention is preferably from at least 0.935 to not more than 0.955 and is more preferably from at least 0.938 to not more than 0.950.

The average circularity of the magnetic toner of the present invention can be adjusted into the indicated range by adjusting the method of producing the magnetic toner and by adjusting the production conditions.

In addition, the glass-transition temperature (Tg) of the magnetic toner of the present invention is preferably from at least 40° C. to not more than 70° C. and more preferably is from at least 50° C. to not more than 70° C. When the glass-transition temperature is from at least 40° C. to not more than 70° C., the storage stability and durability can be improved while maintaining an excellent fixing performance.

Examples of methods for producing the magnetic toner of the present invention are provided below, but there is no intent to limit the production method to these.

The magnetic toner of the present invention can be produced by any known method that enables adjustment of the coverage ratio A, a coefficient of variation on the coverage ratio A and B/A and that preferably has a step in which the average circularity can be adjusted, while the other production steps are not particularly limited.

The following method is a favorable example of such a production method. First, the binder resin, release agent and magnetic body and as necessary other raw materials, e.g., a wax and a charge control agent, are thoroughly mixed using a mixer such as a Henschel mixer or ball mill and are then melted, worked, and kneaded using a heated kneading apparatus such as a roll, kneader, or extruder to compatibilize the resins with each other.

The obtained melted and kneaded material is cooled and solidified and then coarsely pulverized, finely pulverized, and classified, and the external additives, e.g., inorganic fine particles, are externally added and mixed into the resulting magnetic toner particles to obtain the magnetic toner.

The mixer used here can be exemplified by the Henschel mixer (Mitsui Mining Co., Ltd.); Supermixer (Kawata Mfg. Co., Ltd.); Ribocone (Okawara Corporation); Nauta mixer, Turbulizer, and Cyclomix (Hosokawa Micron Corporation); Spiral Pin Mixer (Pacific Machinery & Engineering Co., Ltd.); Loedige Mixer (Matsubo Corporation); and Nobilta (Hosokawa Micron Corporation).

The aforementioned kneading apparatus can be exemplified by the KRC Kneader (Kurimoto, Ltd.); Buss Ko-Kneader (Buss Corp.); TEM extruder (Toshiba Machine Co., Ltd.); TEX twin-screw kneader (The Japan Steel Works, Ltd.); PCM Kneader (Ikegai Ironworks Corporation); three-roll mills, mixing roll mills, kneaders (Inoue Manufacturing Co., Ltd.); Kneadex (Mitsui Mining Co., Ltd.); model MS pressure kneader and Kneader-Ruder (Moriyama Mfg. Co., Ltd.); and Banbury mixer (Kobe Steel, Ltd.).

The aforementioned pulverizer can be exemplified by the Counter Jet Mill, Micron Jet, and Inomizer (Hosokawa Micron Corporation); IDS mill and PJM Jet Mill (Nippon Pneumatic Mfg. Co., Ltd.); Cross Jet Mill (Kurimoto, Ltd.); Ulmax (Nisso Engineering Co., Ltd.); SK Jet-O-Mill (Seishin Enterprise Co., Ltd.); Kryptron (Kawasaki Heavy Industries, Ltd.); Turbo Mill (Turbo Kogyo Co., Ltd.); and Super Rotor (Nisshin Engineering Inc.).

Among the preceding, the average circularity can be controlled by adjusting the exhaust gas temperature during micropulverization using a Turbo Mill. A lower exhaust gas temperature (for example, no more than 40° C.) provides a smaller value for the average circularity while a higher exhaust gas temperature (for example, around 50° C.) provides a higher value for the average circularity.

The aforementioned classifier can be exemplified by the Classiel, Micron Classifier, and Spedic Classifier (Seishin Enterprise Co., Ltd.); Turbo Classifier (Nisshin Engineering Inc.); Micron Separator, Turboplex (ATP), and TSP Separator (Hosokawa Micron Corporation); Elbow Jet (Nittetsu Mining Co., Ltd.); Dispersion Separator (Nippon Pneumatic Mfg. Co., Ltd.); and YM Microcut (Yasukawa Shoji Co., Ltd.).

Screening devices that can be used to screen the coarse particles can be exemplified by the Ultrasonic (Koei Sangyo Co., Ltd.), Rezona Sieve and Gyro-Sifter (Tokuju Corporation), Vibrasonic System (Dalton Co., Ltd.), Soniclean (Sintokogio, Ltd.), Turbo Screener (Turbo Kogyo Co., Ltd.), Microsifter (Makino Mfg. Co., Ltd.), and circular vibrating sieves.

A known mixing process apparatus, e.g., the mixers described above, can be used for the external addition and mixing of the inorganic fine particles; however, an apparatus as shown in FIG. **2** is preferred from the standpoint of enabling facile control of the coverage ratio A, B/A, and the coefficient of variation on the coverage ratio A.

FIG. **2** is a schematic diagram that shows an example of a mixing process apparatus that can be used to carry out the external addition and mixing of the inorganic fine particles used by the present invention.

This mixing process apparatus readily brings about fixing of the inorganic fine particles to the magnetic toner particle surface because it has a structure that applies shear in a narrow clearance region to the magnetic toner particles and the inorganic fine particles.

Furthermore, as described below, the coverage ratio A, B/A, and coefficient of variation on the coverage ratio A are easily controlled into the ranges preferred for the present invention because circulation of the magnetic toner particles and inorganic fine particles in the axial direction of the rotating member is facilitated and because a thorough and uniform mixing is facilitated prior to the development of fixing.

On the other hand, FIG. **3** is a schematic diagram that shows an example of the structure of the stirring member used in the aforementioned mixing process apparatus.

The external addition and mixing process for the inorganic fine particles is described below using FIGS. **2** and **3**.

This mixing process apparatus that carries out external addition and mixing of the inorganic fine particles has a rotating member **2**, on the surface of which at least a plurality of stirring members **3** are disposed; a drive member **8**, which drives the rotation of the rotating member; and a main casing **1**, which is disposed to have a gap with the stirring members **3**.

It is important that the gap (clearance) between the inner circumference of the main casing **1** and the stirring member **3** be maintained constant and very small in order to apply a uniform shear to the magnetic toner particles and facilitate the fixing of the inorganic fine particles to the magnetic toner particle surface.

The diameter of the inner circumference of the main casing **1** in this apparatus is not more than twice the diameter of the outer circumference of the rotating member **2**. In FIG. **2**, an example is shown in which the diameter of the inner circumference of the main casing **1** is 1.7-times the diameter of the outer circumference of the rotating member **2** (the trunk diameter provided by subtracting the stirring member **3** from the rotating member **2**). When the diameter of the inner circumference of the main casing **1** is not more than twice the diameter of the outer circumference of the rotating member **2**, impact force is satisfactorily applied to the magnetic toner particles since the processing space in which forces act on the magnetic toner particles is suitably limited.

In addition, it is important that the aforementioned clearance be adjusted in conformity to the size of the main casing. Viewed from the standpoint of the application of adequate shear to the magnetic toner particles, it is important that the clearance be made from about at least 1% to not more than 5% of the diameter of the inner circumference of the main casing **1**. Specifically, when the diameter of the inner circumference of the main casing **1** is approximately 130 mm, the clearance is preferably made approximately from at least 2 mm to not more than 5 mm; when the diameter of the inner circumference of the main casing **1** is about 800 mm, the clearance is preferably made approximately from at least 10 mm to not more than 30 mm.

In the process of the external addition and mixing of the inorganic fine particles in the present invention, mixing and external addition of the inorganic fine particles to the magnetic toner particle surface are performed using the mixing process apparatus by rotating the rotating member **2** by the drive member **8** and stirring and mixing the magnetic toner particles and inorganic fine particles that have been introduced into the mixing process apparatus.

As shown in FIG. **3**, at least a portion of the plurality of stirring members **3** is formed as a forward transport stirring member **3***a* that, accompanying the rotation of the rotating member **2**, transports the magnetic toner particles and inorganic fine particles in one direction along the axial direction of the rotating member. In addition, at least a portion of the plurality of stirring members **3** is formed as a back transport stirring member **3***b* that, accompanying the rotation of the rotating member **2**, returns the magnetic toner particles and inorganic fine particles in the other direction along the axial direction of the rotating member.

Here, when the raw material inlet port **5** and the product discharge port **6** are disposed at the two ends of the main casing **1**, as in FIG. **2**, the direction toward the product discharge port **6** from the raw material inlet port **5** (the direction to the right in FIG. **2**) is the "forward direction".

That is, as shown in FIG. **3**, the face of the forward transport stirring member **3***a* is tilted so as to transport the magnetic toner particles in the forward direction (**13**). On the other hand, the face of the back transport stirring member **3***b* is tilted so as to transport the magnetic toner particles and the inorganic fine particles in the back direction (**12**).

By doing this, the external addition of the inorganic fine particles to the surface of the magnetic toner particles and mixing are carried out while repeatedly performing transport in the "forward direction" (**13**) and transport in the "back direction" (**12**).

In addition, with regard to the stirring members **3***a*, **3***b*, a plurality of members disposed at intervals in the circumferential direction of the rotating member **2** form a set. In the example shown in FIG. **3**, two members at an interval of 180° with each other form a set of the stirring members **3***a*, **3***b* on the rotating member **2**, but a larger number of members may form a set, such as three at an interval of 120° or four at an interval of 90°.

In the example shown in FIG. **3**, a total of twelve stirring members **3***a*, **3***b* are formed at an equal interval.

Furthermore, D in FIG. **3** indicates the width of a stirring member and d indicates the distance that represents the overlapping portion of a stirring member. In FIG. **3**, D is preferably a width that is approximately from at least 20% to not more than 30% of the length of the rotating member **2**, when considered from the standpoint of bringing about an efficient transport of the magnetic toner particles and inorganic fine particles in the forward direction and back direction. FIG. **3** shows an example in which D is 23%. Furthermore, with regard to the stirring members **3***a* and **3***b*, when an extension line is drawn in the perpendicular direction from the location of the end of the stirring member **3***a*, a certain overlapping portion d of the stirring member with the stirring member **3***b* is preferably present. This serves to efficiently apply shear to the magnetic toner particles. This d is preferably from at least 10% to not more than 30% of D from the standpoint of the application of shear.

In addition to the shape shown in FIG. **3**, the blade shape may be—insofar as the magnetic toner particles can be transported in the forward direction and back direction and the clearance is retained—a shape having a curved surface or a paddle structure in which a distal blade element is connected to the rotating member **2** by a rod-shaped arm.

The present invention will be described in additional detail herebelow with reference to the schematic diagrams of the apparatus shown in FIGS. **2** and **3**.

The apparatus shown in FIG. **2** has a rotating member **2**, which has at least a plurality of stirring members **3** disposed on its surface; a drive member **8** that drives the rotation of the rotating member **2**; a main casing **1**, which is disposed forming a gap with the stirring members **3**; and a jacket **4**, in which a heat transfer medium can flow and which resides on the inside of the main casing **1** and at the end surface **10** of the rotating member.

In addition, the apparatus shown in FIG. **2** has a raw material inlet port **5**, which is formed on the upper side of the main casing **1** for the purpose of introducing the magnetic toner particles and the inorganic fine particles, and a product discharge port **6**, which is formed on the lower side of the main casing **1** for the purpose of discharging, from the main casing to the outside, the magnetic toner that has been subjected to the external addition and mixing process.

The apparatus shown in FIG. **2** also has a raw material inlet port inner piece **16** inserted in the raw material inlet port **5** and a product discharge port inner piece **17** inserted in the product discharge port **6**.

In the present invention, the raw material inlet port inner piece **16** is first removed from the raw material inlet port **5** and the magnetic toner particles are introduced into the processing space **9** from the raw material inlet port **5**. Then, the

inorganic fine particles are introduced into the processing space **9** from the raw material inlet port **5** and the raw material inlet port inner piece **16** is inserted. The rotating member **2** is subsequently rotated by the drive member **8** (**11** represents the direction of rotation), and the thereby introduced material to be processed is subjected to the external addition and mixing process while being stirred and mixed by the plurality of stirring members **3** disposed on the surface of the rotating member **2**.

The sequence of introduction may also be introduction of the inorganic fine particles through the raw material inlet port **5** first and then introduction of the magnetic toner particles through the raw material inlet port **5**. In addition, the magnetic toner particles and the inorganic fine particles may be mixed in advance using a mixer such as a Henschel mixer and the mixture may thereafter be introduced through the raw material inlet port **5** of the apparatus shown in FIG. **2**.

More specifically, with regard to the conditions for the external addition and mixing process, controlling the power of the drive member **8** to from at least 0.2 W/g to not more than 2.0 W/g is preferred in terms of obtaining the coverage ratio A, B/A, and coefficient of variation on the coverage ratio A specified by the present invention. Controlling the power of the drive member **8** to from at least 0.6 W/g to not more than 1.6 W/g is more preferred.

When the power is lower than 0.2 W/g, it is difficult to obtain a high coverage ratio A, and B/A tends to be too low. On the other hand, B/A tends to be too high when 2.0 W/g is exceeded.

The processing time is not particularly limited, but is preferably from at least 3 minutes to not more than 10 minutes. When the processing time is shorter than 3 minutes, B/A tends to be low and a large coefficient of variation on the coverage ratio A is prone to occur. On the other hand, when the processing time exceeds 10 minutes, B/A conversely tends to be high and the temperature within the apparatus is prone to rise.

The rotation rate of the stirring members during external addition and mixing is not particularly limited; however, when, for the apparatus shown in FIG. **2**, the volume of the processing space **9** in the apparatus is 2.0×10^{-3} m^3, the rpm of the stirring members—when the shape of the stirring members **3** is as shown in FIG. **3**—is preferably from at least 1000 rpm to not more than 3000 rpm. The coverage ratio A, B/A, and coefficient of variation on the coverage ratio A as specified for the present invention are readily obtained at from at least 1000 rpm to not more than 3000 rpm.

A particularly preferred processing method for the present invention has a pre-mixing step prior to the external addition and mixing process step. Inserting a pre-mixing step achieves a very uniform dispersion of the inorganic fine particles on the magnetic toner particle surface, and as a result a high coverage ratio A is readily obtained and the coefficient of variation on the coverage ratio A is readily reduced.

More specifically, the pre-mixing processing conditions are preferably a power of the drive member **8** of from at least 0.06 W/g to not more than 0.20 W/g and a processing time of from at least 0.5 minutes to not more than 1.5 minutes. It is difficult to obtain a satisfactorily uniform mixing in the pre-mixing when the loaded power is below 0.06 W/g or the processing time is shorter than 0.5 minutes for the pre-mixing processing conditions. When, on the other hand, the loaded power is higher than 0.20 W/g or the processing time is longer than 1.5 minutes for the pre-mixing processing conditions, the inorganic fine particles may become fixed to the magnetic toner particle surface before a satisfactorily uniform mixing has been achieved.

After the external addition and mixing process has been finished, the product discharge port inner piece **17** in the product discharge port **6** is removed and the rotating member **2** is rotated by the drive member **8** to discharge the magnetic toner from the product discharge port **6**. As necessary, coarse particles and so forth may be separated from the obtained magnetic toner using a screen or sieve, for example, a circular vibrating screen, to obtain the magnetic toner.

An example of an image-forming apparatus that can advantageously use the magnetic toner of the present invention is specifically described below with reference to FIG. **1**. In FIG. **1**, **100** is an electrostatic latent image-bearing member (also referred to below as a photosensitive member), and the following, inter alia, are disposed on its circumference: a charging member (charging roller) **117**, a developing device **140** having a toner-carrying member **102**, a transfer member (transfer charging roller) **114**, a cleaner container **116**, a fixing unit **126**, and a pick-up roller **124**. The electrostatic latent image-bearing member **100** is charged by the charging roller **117**. Photoexposure is performed by irradiating the electrostatic latent image-bearing member **100** with laser light from a laser generator **121** to form an electrostatic latent image corresponding to the intended image. The electrostatic latent image on the electrostatic latent image-bearing member **100** is developed by the developing device **140** with a monocomponent toner to provide a toner image, and the toner image is transferred onto a transfer material by the transfer roller **114**, which contacts the electrostatic latent image-bearing member with the transfer material interposed therebetween. The toner image-bearing transfer material is conveyed to the fixing unit **126** and fixing on the transfer material is carried out. In addition, the magnetic toner remaining to some extent on the electrostatic latent image-bearing member is scraped off by the cleaning blade and is stored in the cleaner container **116**.

The methods for measuring the various properties referenced by the present invention are described below.

<Calculation of the Coverage Ratio A>

The coverage ratio A is calculated in the present invention by analyzing, using Image-Pro Plus ver. **5.0** image analysis software (Nippon Roper Kabushiki Kaisha), the image of the magnetic toner surface taken with Hitachi's S-4800 ultrahigh resolution field emission scanning electron microscope (Hitachi High-Technologies Corporation). The conditions for image acquisition with the S-4800 are as follows.

(1) Specimen Preparation

An electroconductive paste is spread in a thin layer on the specimen stub (15 mm×6 mm aluminum specimen stub) and the magnetic toner is sprayed onto this. Additional blowing with air is performed to remove excess magnetic toner from the specimen stub and carry out thorough drying. The specimen stub is set in the specimen holder and the specimen stub height is adjusted to 36 mm with the specimen height gauge.

(2) Setting the Conditions for Observation with the S-4800

The coverage ratio A is calculated using the image obtained by backscattered electron imaging with the S-4800. The coverage ratio A can be measured with excellent accuracy using the backscattered electron image because the inorganic fine particles are charged up less than is the case with the secondary electron image.

Introduce liquid nitrogen to the brim of the anti-contamination trap located in the S-4800 housing and allow to stand for 30 minutes. Start the "PC-SEM" of the S-4800 and perform flashing (the FE tip, which is the electron source, is cleaned). Click the acceleration voltage display area in the control panel on the screen and press the [flashing] button to open the flashing execution dialog. Confirm a flashing intensity of 2 and execute. Confirm that the emission current due to

flashing is 20 to 40 μA. Insert the specimen holder in the specimen chamber of the S-4800 housing. Press [home] on the control panel to transfer the specimen holder to the observation position.

Click the acceleration voltage display area to open the HV setting dialog and set the acceleration voltage to [0.8 kV] and the emission current to [20 μA]. In the [base] tab of the operation panel, set signal selection to [SE]; select [upper (U)] and [+BSE] for the SE detector; and select [L.A. 100] in the selection box to the right of [+BSE] to go into the observation mode using the backscattered electron image. Similarly, in the [base] tab of the operation panel, set the probe current of the electron optical system condition block to [Normal]; set the focus mode to [UHR]; and set WD to [3.0 mm]. Push the [ON] button in the acceleration voltage display area of the control panel and apply the acceleration voltage.

(3) Calculation of the Number-Average Particle Diameter (D1) of the Magnetic Toner

Set the magnification to 5000× (5 k) by dragging within the magnification indicator area of the control panel. Turn the [COARSE] focus knob on the operation panel and perform adjustment of the aperture alignment where some degree of focus has been obtained. Click [Align] in the control panel and display the alignment dialog and select [beam]. Migrate the displayed beam to the center of the concentric circles by turning the STIGMA/ALIGNMENT knobs (X, Y) on the operation panel. Then select [aperture] and turn the STIGMA/ALIGNMENT knobs (X, Y) one at a time and adjust so as to stop the motion of the image or minimize the motion. Close the aperture dialog and focus with the autofocus. Focus by repeating this operation an additional two times.

After this, determine the number-average particle diameter (D1) by measuring the particle diameter at 300 magnetic toner particles. The particle diameter of the individual particle is taken to be the maximum diameter when the magnetic toner particle is observed.

(4) Focus Adjustment

For particles with a number-average particle diameter (D1) obtained in (3) of ±0.1 μm, with the center of the maximum diameter adjusted to the center of the measurement screen, drag within the magnification indication area of the control panel to set the magnification to 10000× (10 k). Turn the [COARSE] focus knob on the operation panel and perform adjustment of the aperture alignment where some degree of focus has been obtained. Click [Align] in the control panel and display the alignment dialog and select [beam]. Migrate the displayed beam to the center of the concentric circles by turning the STIGMA/ALIGNMENT knobs (X, Y) on the operation panel. Then select [aperture] and turn the STIGMA/ALIGNMENT knobs (X, Y) one at a time and adjust so as to stop the motion of the image or minimize the motion. Close the aperture dialog and focus using autofocus. Then set the magnification to 50000× (50 k); carry out focus adjustment as above using the focus knob and the STIGMA/ALIGNMENT knob; and re-focus using autofocus. Focus by repeating this operation. Here, because the accuracy of the coverage ratio measurement is prone to decline when the observation plane has a large tilt angle, carry out the analysis by making a selection with the least tilt in the surface by making a selection during focus adjustment in which the entire observation plane is simultaneously in focus.

(5) Image Capture

Carry out brightness adjustment using the ABC mode and take a photograph with a size of 640×480 pixels and store. Carry out the analysis described below using this image file. Take one photograph for each magnetic toner particle and obtain images for at least 30 magnetic toner particles.

(6) Image Analysis

The coverage ratio A is calculated in the present invention using the analysis software indicated below by subjecting the image obtained by the above-described procedure to binarization processing. When this is done, the above-described single image is divided into 12 squares and each is analyzed. However, when an inorganic fine particle with a particle diameter greater than or equal to 50 nm is present within a partition, calculation of the coverage ratio A is not performed for this partition.

The analysis conditions with the Image-Pro Plus ver. 5.0 image analysis software are as follows.

Software: Image-ProPlus5.1J

From "measurement" in the tool-bar, select "count/size" and then "option" and set the binarization conditions. Select 8 links in the object extraction option and set smoothing to 0. In addition, preliminary screening, fill vacancies, and envelope are not selected and the "exclusion of boundary line" is set to "none". Select "measurement items" from "measurement" in the tool-bar and enter 2 to 10^7 for the area screening range.

The coverage ratio is calculated by marking out a square zone. Here, the area (C) of the zone is made 24000 to 26000 pixels. Automatic binarization is performed by "processing"-binarization and the total area (D) of the silica-free zone is calculated.

The coverage ratio a is calculated using the following formula from the area C of the square zone and the total area D of the silica-free zone.

$$\text{coverage ratio } a(\%)=100-(D/C\times 100)$$

As noted above, calculation of the coverage ratio a is carried out for at least 30 magnetic toner particles. The average value of all the obtained data is taken to be the coverage ratio A of the present invention.

<The Coefficient of Variation on the Coverage Ratio A>

The coefficient of variation on the coverage ratio A is determined in the present invention as follows. The coefficient of variation on the coverage ratio A is obtained using the following formula letting σ(A) be the standard deviation on all the coverage ratio data used in the calculation of the coverage ratio A described above.

$$\text{coefficient of variation}(\%)=\{\sigma(A)/A\}\times 100$$

<Calculation of the Coverage Ratio B>

The coverage ratio B is calculated by first removing the unfixed inorganic fine particles on the magnetic toner surface and thereafter carrying out the same procedure as followed for the calculation of the coverage ratio A.

(1) Removal of the Unfixed Inorganic Fine Particles

The unfixed inorganic fine particles are removed as described below. The present inventors investigated and then set these removal conditions in order to thoroughly remove the inorganic fine particles other than those embedded in the toner surface.

As an example, FIG. **7** shows the relationship between the ultrasound dispersion time and the coverage ratio calculated post-ultrasound dispersion, for magnetic toners in which the coverage ratio A was brought to 46% using the apparatus shown in FIG. **2** at three different external addition intensities. FIG. **7** was constructed by calculating, using the same procedure as for the calculation of coverage ratio A as described above, the coverage ratio of a magnetic toner provided by removing the inorganic fine particles by ultrasound dispersion by the method described below and then drying.

FIG. 7 demonstrates that the coverage ratio declines in association with removal of the inorganic fine particles by ultrasound dispersion and that, for all of the external addition intensities, the coverage ratio is brought to an approximately constant value by ultrasound dispersion for 20 minutes. Based on this, ultrasound dispersion for 30 minutes was regarded as providing a thorough removal of the inorganic fine particles other than the inorganic fine particles embedded in the toner surface and the thereby obtained coverage ratio was defined as coverage ratio B.

Considered in greater detail, 16.0 g of water and 4.0 g of Contaminon N (a neutral detergent from Wako Pure Chemical Industries, Ltd., product No. 037-10361) are introduced into a 30 mL glass vial and are thoroughly mixed. 1.50 g of the magnetic toner is introduced into the resulting solution and the magnetic toner is completely submerged by applying a magnet at the bottom. After this, the magnet is moved around in order to condition the magnetic toner to the solution and remove air bubbles.

The tip of a UH-50 ultrasound oscillator (from SMT Co., Ltd., the tip used is a titanium alloy tip with a tip diameter of 6 mm) is inserted so it is in the center of the vial and resides at a height of 5 mm from the bottom of the vial, and the inorganic fine particles are removed by ultrasound dispersion. After the application of ultrasound for 30 minutes, the entire amount of the magnetic toner is removed and dried. During this time, as little heat as possible is applied while carrying out vacuum drying at not more than 30° C.

(2) Calculation of the Coverage Ratio B

After the drying as described above, the coverage ratio of the magnetic toner is calculated as for the coverage ratio A described above, to obtain the coverage ratio B.

<Method for Measuring the Weight-Average Particle Diameter (D4) and the Particle Size Distribution of the Magnetic Toner>

The weight-average particle diameter (D4) of the magnetic toner is calculated as follows. The measurement instrument used is a "Coulter Counter Multisizer 3" (registered trademark, from Beckman Coulter, Inc.), a precision particle size distribution measurement instrument operating on the pore electrical resistance principle and equipped with a 100 μm aperture tube. The measurement conditions are set and the measurement data are analyzed using the accompanying dedicated software, i.e., "Beckman Coulter Multisizer 3 Version 3.51" (from Beckman Coulter, Inc.). The measurements are carried at 25000 channels for the number of effective measurement channels.

The aqueous electrolyte solution used for the measurements is prepared by dissolving special-grade sodium chloride in ion-exchanged water to provide a concentration of about 1 mass % and, for example, "ISOTON II" (from Beckman Coulter, Inc.) can be used.

The dedicated software is configured as follows prior to measurement and analysis.

In the "modify the standard operating method (SOM)" screen in the dedicated software, the total count number in the control mode is set to 50000 particles; the number of measurements is set to 1 time; and the Kd value is set to the value obtained using "standard particle 10.0 μm" (from Beckman Coulter, Inc.). The threshold value and noise level are automatically set by pressing the "threshold value/noise level measurement button". In addition, the current is set to 1600 μA; the gain is set to 2; the electrolyte is set to ISOTON II; and a check is entered for the "post-measurement aperture tube flush".

In the "setting conversion from pulses to particle diameter" screen of the dedicated software, the bin interval is set to logarithmic particle diameter; the particle diameter bin is set to 256 particle diameter bins; and the particle diameter range is set to from 2 μm to 60 μm.

The specific measurement procedure is as follows.

(1) Approximately 200 mL of the above-described aqueous electrolyte solution is introduced into a 250-mL roundbottom glass beaker intended for use with the Multisizer 3 and this is placed in the sample stand and counterclockwise stirring with the stirrer rod is carried out at 24 rotations per second. Contamination and air bubbles within the aperture tube have previously been removed by the "aperture flush" function of the dedicated software.

(2) Approximately 30 mL of the above-described aqueous electrolyte solution is introduced into a 100-mL flatbottom glass beaker. To this is added as dispersant about 0.3 mL of a dilution prepared by the approximately three-fold (mass) dilution with ion-exchanged water of "Contaminon N" (a 10 mass % aqueous solution of a neutral pH 7 detergent for cleaning precision measurement instrumentation, comprising a nonionic surfactant, anionic surfactant, and organic builder, from Wako Pure Chemical Industries, Ltd.).

(3) An "Ultrasonic Dispersion System Tetora 150" (Nikkaki Bios Co., Ltd.) is prepared; this is an ultrasound disperser with an electrical output of 120 W and is equipped with two oscillators (oscillation frequency=50 kHz) disposed such that the phases are displaced by 180°. Approximately 3.3 L of ion-exchanged water is introduced into the water tank of this ultrasound disperser and approximately 2 mL of Contaminon N is added to the water tank.

(4) The beaker described in (2) is set into the beaker holder opening on the ultrasound disperser and the ultrasound disperser is started. The height of the beaker is adjusted in such a manner that the resonance condition of the surface of the aqueous electrolyte solution within the beaker is at a maximum.

(5) While the aqueous electrolyte solution within the beaker set up according to (4) is being irradiated with ultrasound, approximately 10 mg of toner is added to the aqueous electrolyte solution in small aliquots and dispersion is carried out. The ultrasound dispersion treatment is continued for an additional 60 seconds. The water temperature in the water bath is controlled as appropriate during ultrasound dispersion to be at least 10° C. and not more than 40° C.

(6) Using a pipette, the dispersed toner-containing aqueous electrolyte solution prepared in (5) is dripped into the roundbottom beaker set in the sample stand as described in (1) with adjustment to provide a measurement concentration of about 5%. Measurement is then performed until the number of measured particles reaches 50000.

(7) The measurement data is analyzed by the previously cited software provided with the instrument and the weight-average particle diameter (D4) is calculated. When set to graph/volume % with the dedicated software, the "average diameter" on the "analysis/volumetric statistical value (arithmetic average)" screen is the weight-average particle diameter (D4).

<Method of Measuring the Average Circularity of the Magnetic Toner>

The average circularity of the magnetic toner according to the present invention is measured with the "FPIA-3000" (Sysmex Corporation), a flow-type particle image analyzer, using the measurement and analysis conditions from the calibration process.

The specific measurement method is as follows. First, approximately 20 mL of ion-exchanged water from which the solid impurities and so forth have previously been removed is

placed in a glass container. To this is added as dispersant about 0.2 mL of a dilution prepared by the approximately three-fold (mass) dilution with ion-exchanged water of "Contaminon N" (a 10 mass % aqueous solution of a neutral pH 7 detergent for cleaning precision measurement instrumentation, comprising a nonionic surfactant, anionic surfactant, and organic builder, from Wako Pure Chemical Industries, Ltd.). Approximately 0.02 g of the measurement sample is also added and a dispersion treatment is carried out for 2 minutes using an ultrasound disperser to provide a dispersion for submission to measurement. Cooling is carried out as appropriate during this treatment so as to provide a dispersion temperature of at least 10° C. and no more than 40° C. The ultrasound disperser used here is a benchtop ultrasonic cleaner/disperser that has an oscillation frequency of 50 kHz and an electrical output of 150 W (for example, a "VS-150" from Velvo-Clear Co., Ltd.); a prescribed amount of ion-exchanged water is introduced into the water tank and approximately 2 mL of the aforementioned Contaminon N is also added to the water tank.

The previously cited flow-type particle image analyzer (fitted with a standard objective lens (10×)) is used for the measurement, and Particle Sheath "PSE-900A" (Sysmex Corporation) is used for the sheath solution. The dispersion prepared according to the procedure described above is introduced into the flow-type particle image analyzer and 3000 of the magnetic toner are measured according to total count mode in HPF measurement mode. The average circularity of the magnetic toner is determined with the binarization threshold value during particle analysis set at 85% and the analyzed particle diameter limited to a circle-equivalent diameter of from at least 1.985 μm to less than 39.69 μm.

For this measurement, automatic focal point adjustment is performed prior to the start of the measurement using reference latex particles (for example, a dilution with ion-exchanged water of "RESEARCH AND TEST PARTICLES Latex Microsphere Suspensions 5200A" from Duke Scientific). After this, focal point adjustment is preferably performed every two hours after the start of measurement.

In the present invention, the flow-type particle image analyzer used had been calibrated by the Sysmex Corporation and had been issued a calibration certificate by the Sysmex Corporation. The measurements are carried out under the same measurement and analysis conditions as when the calibration certificate was received, with the exception that the analyzed particle diameter is limited to a circle-equivalent diameter of from at least 1.985 μm to less than 39.69 μm.

The "FPIA-3000" flow-type particle image analyzer (Sysmex Corporation) uses a measurement principle based on taking a still image of the flowing particles and performing image analysis. The sample added to the sample chamber is delivered by a sample suction syringe into a flat sheath flow cell. The sample delivered into the flat sheath flow is sandwiched by the sheath liquid to form a flat flow. The sample passing through the flat sheath flow cell is exposed to stroboscopic light at an interval of 1/60 seconds, thus enabling a still image of the flowing particles to be photographed. Moreover, since flat flow is occurring, the photograph is taken under in-focus conditions. The particle image is photographed with a CCD camera; the photographed image is subjected to image processing at an image processing resolution of 512×512 pixels (0.37×0.37 μm per pixel); contour definition is performed on each particle image; and, among other things, the projected area S and the periphery length L are measured on the particle image.

The circle-equivalent diameter and the circularity are then determined using this area S and periphery length L. The circle-equivalent diameter is the diameter of the circle that has the same area as the projected area of the particle image. The circularity is defined as the value provided by dividing the circumference of the circle determined from the circle-equivalent diameter by the periphery length of the particle's projected image and is calculated using the following formula.

$$\text{circularity}=2\times(\pi\times S)^{1/2}/L$$

The circularity is 1.000 when the particle image is a circle, and the value of the circularity declines as the degree of irregularity in the periphery of the particle image increases. After the circularity of each particle has been calculated, 800 are fractionated out in the circularity range of 0.200 to 1.000; the arithmetic average value of the obtained circularities is calculated; and this value is used as the average circularity.

<Method for Measuring the Peak Molecular Weight (Mp) of the Magnetic Toners and Resins>

The peak molecular weight (Mp) of the magnetic toners and resins is measured using gel permeation chromatography (GPC) under the following conditions.

The column is stabilized in a heated chamber at 40° C., and tetrahydrofuran (THF) is introduced as solvent at a flow rate of 1 mL per minute into the column at this temperature. For the column, a combination of a plurality of commercially available polystyrene gel columns is favorably used to accurately measure the molecular weight range of 1×10^3 to 2×10^6. The combination may be formed of Shodex GPC KF-801, 802, 803, 804, 805, 806 and 807 from Showa Denko Kabushiki Kaisha and the combination of TSKgel G1000H (HXL), G2000H(HXL), G3000H(HXL), G4000H(HXL), G5000H(HXL), G6000H(HXL), G7000H(HXL), and TSK-guard column from Tosoh Corporation, while a 7-column train of Shodex KF-801, 802, 803, 804, 805, 806, and 807 from Showa Denko Kabushiki Kaisha is preferred.

On the other hand, the magnetic toner or resin is dispersed and dissolved in tetra hydrofuran (THF) and allowed to stand overnight and is then filtered on a sample treatment filter (for example, a MyShoriDisk H-25-2 with a pore size of 0.2 to 0.5 μm (Tosoh Corporation)) and the filtrate is used for the sample. 50 to 200 μL of the THF solution of the resin, which has been adjusted to bring the resin component to 0.5 to 5 mg/mL for the sample concentration, is injected to carry out the measurement. An RI (refractive index) detector is used for the detector.

To measure the molecular weight of the sample, the molecular weight distribution possessed by the sample is calculated from the relationship between the number of counts and the logarithmic value on a calibration curve constructed using several different monodisperse polystyrene standard samples. The standard polystyrene samples used to construct the calibration curve can be exemplified by samples with a molecular weight of 6×10^2, 2.1×10^2, 4×10^2, 1.75×10^4, 5.1×10^4, 1.1×10^5, 3.9×10^5, 8.6×10^5, 2×10^6, and 4.48×10^6 from the Pressure Chemical Company or Tosoh Corporation, and standard polystyrene samples at approximately 10 points or more are used.

<Method of Measuring the Number-Average Particle Diameter of the Primary Particles of the Inorganic Fine Particles>

The number-average particle diameter of the primary particles of the inorganic fine particles is calculated from the inorganic fine particle image on the magnetic toner surface taken with Hitachi's S-4800 ultrahigh resolution field emission scanning electron microscope (Hitachi High-Technologies Corporation). The conditions for image acquisition with the S-4800 are as follows.

The same steps (1) to (3) as described above in "Calculation of the coverage ratio A" are carried out; focusing is performed by carrying out focus adjustment at a 50000× magnification of the magnetic toner surface as in (4); and the brightness is then adjusted using the ABC mode. This is followed by bringing the magnification to 100000×; performing focus adjustment using the focus knob and STIGMA/ALIGNMENT knobs as in (4); and focusing using autofocus. The focus adjustment process is repeated to achieve focus at 100000×.

After this, the particle diameter is measured on at least 300 inorganic fine particles on the magnetic toner surface and the number-average particle diameter (D1) is determined. Here, because the inorganic fine particles are also present as aggregates, the maximum diameter is determined on what can be identified as the primary particle, and the primary particle number-average particle diameter (D1) is obtained by taking the arithmetic average of the obtained maximum diameters.

EXAMPLES

The present invention is more specifically described through the examples and comparative examples provided below, but the present invention is in no way restricted to these. The number of parts in the blends described below are mass parts in all instances.

Production Example for Binder Resin 1

300 mass parts of xylene was introduced into a four-neck flask and was heated under reflux and a liquid mixture of 82.0 mass parts of styrene, 18.0 mass parts of n-butyl acrylate, and 4.0 mass parts of di-tert-butyl peroxide that is a polymerization initiator was added dropwise over 5 hours to obtain a low molecular weight polymer (L-1) solution.

180 mass parts of degassed water and 20 mass parts of a 2 mass % aqueous polyvinyl alcohol solution were introduced into a four-neck flask; a liquid mixture of 75.0 mass parts of styrene, 25.0 mass parts of n-butyl acrylate, 0.005 mass parts of divinylbenzene, and 3.0 mass parts of 2,2-bis(4,4-di-tert-butylperoxycyclohexyl)propane (10-hour half-life temperature: 92° C.) was thereafter added; and stirring was carried out to yield a suspension. After the interior of the flask had been thoroughly replaced with polymerization was carried out; after holding for 24 hours, 1.0 mass part of benzoyl peroxide (10-hour half-life temperature: 72° C.) was added and holding was continued for another 12 hours to finish the polymerization of a high molecular weight polymer (H-1).

25 mass parts of the high molecular weight polymer (H-1) was introduced into 300 mass parts of the uniform solution of the low molecular weight polymer (L-1); thorough mixing was performed under reflux; and the organic solvent was then removed to obtain styrene binder resin 1. The acid value and hydroxyl value of this binder resin were 0 mg KOH/g, and it had a glass-transition temperature (Tg) of 58° C., an Mp of 6000, and a THF-insoluble matter of 0 mass %. The properties of binder resin 1 are shown in Table 2.

Production Example for Binder Resin 2

Binder resin 2 was obtained proceeding as in the Production Example for Binder Resin 1, with the exception that the amount of the polymerization initiator used during the production of the low molecular weight polymer in the Production Example for Binder Resin 1 was changed from 4.0 mass parts to 4.5 mass parts. The properties of binder resin 2 are shown in Table 2.

Production Example for Binder Resin 3

Binder resin 3 was obtained proceeding as in the Production Example for Binder Resin 1, with the exception that the amount of the polymerization initiator used during the production of the low molecular weight polymer in the Production Example for Binder Resin 1 was changed from 4.0 mass parts to 3.5 mass parts. The properties of binder resin 3 are shown in Table 2.

Production Example for Binder Resin 4

Binder resin 4 was obtained proceeding as in the Production Example for Binder Resin 1, with the exception that the amount of the polymerization initiator used during the production of the low molecular weight polymer in the Production Example for Binder Resin 1 was changed from 4.0 mass parts to 4.2 mass parts. The properties of binder resin 4 are shown in Table 2.

Production Example for Binder Resin 5

Binder resin 5 was obtained proceeding as in the Production Example for Binder Resin 1, with the exception that the amount of the polymerization initiator used during the production of the low molecular weight polymer in the Production Example for Binder Resin 1 was changed from 4.0 mass parts to 3.7 mass parts. The properties of binder resin 5 are shown in Table 2.

Production Example for Comparative Binder Resin 1

Comparative binder resin 1 was obtained proceeding as in the Production Example for Binder Resin 1, with the exception that the amount of the polymerization initiator used during the production of the low molecular weight polymer in the Production Example for Binder Resin 1 was changed from 4.0 mass parts to 4.7 mass parts. The properties of comparative binder resin 1 are shown in Table 2.

Production Example for Comparative Binder Resin 2

Comparative binder resin 2 was obtained proceeding as in the Production Example for Binder Resin 1, with the exception that the amount of the polymerization initiator used during the production of the low molecular weight polymer in the Production Example for Binder Resin 1 was changed from 4.0 mass parts to 3.2 mass parts. The properties of comparative binder resin 2 are shown in Table 2.

Magnetic Body 1 Production Example

An aqueous solution containing ferrous hydroxide was prepared by mixing the following in an aqueous solution of ferrous sulfate: a sodium hydroxide solution at 1.1 equivalent with reference to the iron and SiO_2 in an amount that provided 1.20 mass % as silicon with reference to the iron. The pH of the aqueous solution was brought to 8.0 and an oxidation reaction was run at 85° C. while blowing in air to prepare a slurry containing seed crystals.

An aqueous ferrous sulfate solution was then added to provide 1.0 equivalent with reference to the amount of the starting alkali (sodium component in the sodium hydroxide) in this slurry and an oxidation reaction was run while blowing in air and maintaining the slurry at pH 8.5 to obtain a slurry containing magnetic iron oxide. This slurry was filtered, washed, dried, and ground to obtain a magnetic body 1 that had a primary particle number-average particle diameter (D1) of 0.22 μm and, for a magnetic field of 795.8 kA/m, a intensity of magnetization of 83.5 Am^2/kg, residual magnetization of 6.3 Am^2/kg, and coercive force of 5.3 kA/m.

Magnetic Toner Particle Production Example 1

binder resin 1 shown in Table 2	100.0 mass parts
release agent 1 shown in Table 1	3.0 mass parts
release agent 8 shown in Table 1	2.0 mass parts
magnetic body 1	95.0 mass parts
charge control agent	1.0 mass part

(azo-iron compound; T-77 (Hodogaya Chemical Co., Ltd.))

The starting materials listed above were preliminarily mixed using an FM10C Henschel mixer (Mitsui Miike

Chemical Engineering Machinery Co., Ltd.). This was followed by kneading with a twin-screw kneader/extruder (PCM-30, Ikegai Ironworks Corporation) set at a rotation rate of 200 rpm with the set temperature being adjusted to provide a direct temperature in the vicinity of the outlet for the kneaded material of 150° C.

The resulting melt-kneaded material was cooled; the cooled melt-kneaded material was coarsely pulverized with a cutter mill; the resulting coarsely pulverized material was finely pulverized using a Turbo Mill T-250 (Turbo Kogyo Co., Ltd.) at a feed rate of 20 kg/hr with the air temperature adjusted to provide an exhaust gas temperature of 38° C.; and classification was performed using a Coanda effect-based multifraction classifier to obtain a magnetic toner particle 1 having a weight-average particle diameter (D**4**) of 7.8 μm. Release agents 1 and 8 are shown in Table 1. The binder resin 1 used is shown in Table 2. The magnetic toner particle 1 is shown in Table 3.

Magnetic Toner Production Example 1

An external addition and mixing process was carried out using the apparatus shown in FIG. **2** on the magnetic toner particle 1 provided by Magnetic Toner Particle Production Example 1.

In this example, the diameter of the inner circumference of the main casing **1** of the apparatus shown in FIG. **2** was 130 mm; the apparatus used had a volume for the processing space **9** of 2.0×10^{-3} m^3; the rated power for the drive member **8** was 5.5 kW; and the stirring member **3** had the shape given in FIG. **3**. The overlap width d in FIG. **3** between the stirring member **3***a* and the stirring member **3***b* was 0.25D with respect to the maximum width D of the stirring member **3**, and the clearance between the stirring member **3** and the inner circumference of the main casing **1** was 3.0 mm.

100 mass parts of magnetic toner particles 1 and 2.00 mass parts of the silica fine particles 1 described below were introduced into the apparatus shown in FIG. **2** having the apparatus structure described above.

Silica fine particles 1 were obtained by treating 100 mass parts of a silica with a BET specific surface area of 130 m^2/g and a primary particle number-average particle diameter (D**1**) of 16 nm with 10 mass parts hexamethyldisilazane and then with 10 mass parts dimethylsilicone oil.

A pre-mixing was carried out after the introduction of the magnetic toner particles and the silica fine particles in order to uniformly mix the magnetic toner particles and the silica fine particles. The pre-mixing conditions were as follows: a drive member **8** power of 0.1 W/g (drive member **8** rotation rate of 150 rpm) and a processing time of 1 minute.

The external addition and mixing process was carried out once pre-mixing was finished. With regard to the conditions for the external addition and mixing process, the processing time was 5 minutes and the peripheral velocity of the outermost end of the stirring member **3** was adjusted to provide a constant drive member **8** power of 1.0 W/g (drive member **8** rotation rate of 1800 rpm). The conditions for the external addition and mixing process are shown in Table 4.

After the external addition and mixing process, the coarse particles were removed using a circular vibrating screen equipped with a screen having a diameter of 500 mm and an aperture of 75 μm to obtain magnetic toner 1. A value of 18 nm was obtained when magnetic toner 1 was submitted to magnification and observation with a scanning electron microscope and the number-average particle diameter of the primary particles of the silica fine particles on the magnetic toner surface was measured. The external addition conditions and properties of magnetic toner 1 are shown in Table 3 and Table 4, respectively.

TABLE 1

	Name	Melting point (° C.)	Number of carbons in the fatty acid	Functionality
Release agent 1	Pentaerythritol tetrabehenate	84.2	C22	4
Release agent 2	Dipentaerythritol hexabehenate	82.7	C22	6
Release agent 3	Pentaerythritol tetraarachidate	79.8	C20	4
Release agent 4	Pentaerythritol tetrastearate	76.5	C18	4
Release agent 5	Dipentaerythritol hexapalmitate	69.1	C16	6
Release agent 6	Pentaerythritol tetralignocerate	87.7	C24	4
Release agent 7	Tribehenin	83.3	C22	3
Release agent 8	Polyethylene wax	77.3	—	0
Release agent 9	Pentaerythritol tetracerotate	93.4	C26	4

TABLE 2

	Type of resin	Main peak molecular weight (mp)	Tg (° C.)
Binder resin 1	Styrene-acrylic resin	6000	58
Binder resin 2	Styrene-acrylic resin	4300	57
Binder resin 3	Styrene-acrylic resin	8100	59
Binder resin 4	Styrene-acrylic resin	5200	58
Binder resin 5	Styrene-acrylic resin	7200	59
Comparative binder resin 1	Styrene-acrylic resin	3800	56
Comparative binder resin 2	Styrene-acrylic resin	8700	60

TABLE 3

	Binder resin	Release agent	Release agent content (mass parts)	Weight-average particle diameter D4 (μm)	Average circularity
Magnetic toner particle 1	Binder resin 1	Release agent 1/ Release agent 8	3/2	7.8	0.944
Magnetic toner particle 2	Binder resin 1	Release agent 1	5	7.9	0.944
Magnetic toner particle 3	Binder resin 2	Release agent 1/ Release agent 8	3/2	7.6	0.945
Magnetic toner particle 4	Binder resin 3	Release agent 1/ Release agent 8	3/2	7.6	0.941
Magnetic toner particle 5	Binder resin 1	Release agent 2/ Release agent 8	3/2	7.7	0.944
Magnetic toner particle 6	Binder resin 1	Release agent 3/ Release agent 8	3/2	7.8	0.944
Magnetic toner particle 7	Binder resin 1	Release agent 4/ Release agent 8	3/2	7.8	0.944
Magnetic toner particle 8	Binder resin 1	Release agent 5/ Release agent 8	3/2	7.9	0.944
Magnetic toner particle 9	Binder resin 1	Release agent 6/ Release agent 9	3/2	7.7	0.944
Magnetic toner particle 10	Comparative binder resin 1	Release agent 1/ Release agent 8	3/2	7.8	0.944
Magnetic toner particle 11	Comparative binder resin 2	Release agent 1/ Release agent 8	3/2	7.6	0.944
Magnetic toner particle 12	Binder resin 1	Release agent 7/ Release agent 8	3/2	7.7	0.944
Magnetic toner particle 13	Binder resin 1	Release agent 8	5	7.6	0.944
Magnetic toner particle 14	Binder resin 1	Release agent 9/ Release agent 8	3/2	7.6	0.944
Magnetic toner particle 15	Binder resin 1	Release agent 1/ Release agent 8	3/2	7.7	0.970
Magnetic toner particle 16	Binder resin 1	Release agent 1/ Release agent 8	3/2	7.9	0.970
Magnetic toner particle 17	Binder resin 1	Release agent 1	6	7.9	0.944
Magnetic toner particle 18	Binder resin 4	Release agent 1/ Release agent 8	3/2	7.8	0.948
Magnetic toner particle 19	Binder resin 5	Release agent 1/ Release agent 8	3/2	7.8	0.942
Magnetic toner particle 20	Binder resin 1	Release agent 1/ Release agent 8	4/1	7.8	0.944
Magnetic toner particle 21	Binder resin 1	Release agent 1/ Release agent 8	1/4	7.8	0.944
Magnetic toner particle 22	Binder resin 1	Release agent 1/ Release agent 8	1/5	7.8	0.944
Magnetic toner particle 23	Binder resin 1	Release agent 1/ Release agent 8	3/2	7.8	0.953
Magnetic toner particle 24	Binder resin 1	Release agent 1/ Release agent 8	3/2	7.8	0.957

TABLE 4-1

Magnetic toner	Magnetic toner particle	Main peak molecular weight (Mp)	Silica fine particles (mass parts)	Titania fine particles (mass parts)	Alumina fine particles (mass parts)	Content of silica fine particles (mass %)	Content of silica fine particles in the fixed inorganic fine particles (mass %)	External addition apparatus	Operating conditions for the external addition apparatus	Operating time by the external addition apparatus	Coverage ratio A (%)	B/A (–)	Coefficient of variation on coverage ratio A (%)
Magnetic toner 1	Magnetic toner particle 1	5800	2.00	—	—	100	100	Apparatus of FIG. 2	1.0 W/g (1800 rpm)	5 min	56.1	0.70	6.6
Magnetic toner 2	Magnetic toner particle 1	5800	1.70	0.30	—	85	85	Apparatus of FIG. 2	1.0 W/g (1800 rpm)	5 min	55.3	0.68	6.9

TABLE 4-1-continued

Magnetic toner	Magnetic toner particle	Main peak molecular weight (Mp)	Silica fine particles (mass parts)	Titania fine particles (mass parts)	Alumina fine particles (mass parts)	Content of silica fine particles (mass %)	Content of silica fine particles in the fixed inorganic fine particles (mass %)	External addition apparatus	Operating conditions for the external addition apparatus	Operating time by the external addition apparatus	Coverage ratio A (%)	B/A (–)	Coefficient of variation on coverage ratio A (%)
Magnetic toner 3	Magnetic toner particle 1	5800	1.70	0.15	0.15	85	85	Apparatus of FIG. 2	1.0 W/g (1800 rpm)	5 min	54.8	0.67	6.9
Magnetic toner 4	Magnetic toner particle 1	5800	1.50	—	—	100	100	Apparatus of FIG. 2	1.0 W/g (1800 rpm)	5 min	46.3	0.72	6.8
Magnetic toner 5	Magnetic toner particle 1	5800	1.28	0.22	—	85	85	Apparatus of FIG. 2	1.0 W/g (1800 rpm)	5 min	46.0	0.71	6.9
Magnetic toner 6	Magnetic toner particle 1	5800	1.28	0.12	0.10	85	85	Apparatus of FIG. 2	1.0 W/g (1800 rpm)	5 min	45.9	0.71	7.0
Magnetic toner 7	Magnetic toner particle 1	5800	2.60	—	—	100	100	Apparatus of FIG. 2	1.0 W/g (1800 rpm)	5 min	69.9	0.68	6.4
Magnetic toner 8	Magnetic toner particle 1	5800	2.25	0.35	—	87	87	Apparatus of FIG. 2	1.0 W/g (1800 rpm)	5 min	69.4	0.68	6.5
Magnetic toner 9	Magnetic toner particle 1	5800	2.25	0.20	0.15	87	87	Apparatus of FIG. 2	1.0 W/g (1800 rpm)	5 min	68.5	0.67	6.7
Magnetic toner 10	Magnetic toner particle 1	5800	1.50	—	—	100	100	Apparatus of FIG. 2	1.6 W/g (2500 rpm)	5 min	46.3	0.84	6.4
Magnetic toner 11	Magnetic toner particle 1	5800	1.50	—	—	100	100	Apparatus of FIG. 2	0.6 W/g (1400 rpm)	5 min	46.3	0.52	7.2
Magnetic toner 12	Magnetic toner particle 1	5800	2.60	—	—	100	100	Apparatus of FIG. 2	1.6 W/g (2500 rpm)	5 min	69.5	0.83	6.0
Magnetic toner 13	Magnetic toner particle 1	5800	2.60	—	—	100	100	Apparatus of FIG. 2	0.6 W/g (1400 rpm)	5 min	69.5	0.52	6.8
Magnetic toner 14	Magnetic toner particle 2	5800	2.00	—	—	100	100	Apparatus of FIG. 2	1.0 W/g (1800 rpm)	5 min	56.1	0.70	6.8
Magnetic toner 15	Magnetic toner particle 1	5800	2.00	—	—	100	100	Apparatus of FIG. 2	No pre-mixing 1.0 W/g (1800 rpm)	5 min	54.9	0.69	9.9
Magnetic toner 16	Magnetic toner particle 3	4100	2.00	—	—	100	100	Apparatus of FIG. 2	1.0 W/g (1800 rpm)	5 min	58.6	0.80	6.7
Magnetic toner 17	Magnetic toner particle 4	7800	2.00	—	—	100	100	Apparatus of FIG. 2	1.0 W/g (1800 rpm)	5 min	53.6	0.66	7.5
Magnetic toner 18	Magnetic toner particle 5	5800	2.00	—	—	100	100	Apparatus of FIG. 2	1.0 W/g (1800 rpm)	5 min	57.8	0.69	7.0
Magnetic toner 19	Magnetic toner particle 6	5800	2.00	—	—	100	100	Apparatus of FIG. 2	1.0 W/g (1800 rpm)	5 min	55.9	0.70	6.8
Magnetic toner 20	Magnetic toner particle 7	5800	2.00	—	—	100	100	Apparatus of FIG. 2	1.0 W/g (1800 rpm)	5 min	55.5	0.70	6.6
Magnetic toner 21	Magnetic toner particle 8	5800	2.00	—	—	100	100	Apparatus of FIG. 2	1.0 W/g (1800 rpm)	5 min	55.9	0.74	6.3
Magnetic toner 22	Magnetic toner particle 9	5800	2.00	—	—	100	100	Apparatus of FIG. 2	1.0 W/g (1800 rpm)	5 min	54.4	0.61	6.4
Magnetic toner 23	Magnetic toner particle 1	5800	2.00	—	—	100	100	Apparatus of FIG. 2	1.0 W/g (1800 rpm)	5 min	58.9	0.73	6.2
Magnetic toner 24	Magnetic toner particle 1	5800	2.00	—	—	100	100	Apparatus of FIG. 2	1.0 W/g (1800 rpm)	5 min	52.2	0.65	8.1

TABLE 4-2

Magnetic toner	Magnetic toner particle	Main peak molecular weight (Mp)	Silica fine particles (mass parts)	Titania fine particles (mass parts)	Alumina fine particles (mass parts)	Content of silica fine particles (mass %)	Content of silica fine particles in the fixed inorganic fine particles (mass %)
Magnetic toner 25	Magnetic toner particle 1	5800	1.70	0.30	—	85	80
Magnetic toner 26	Magnetic toner particle 1	5800	1.70	0.30	—	85	90
Magnetic toner 27	Magnetic toner particle 18	5000	2.00	—	—	100	100
Magnetic toner 28	Magnetic toner particle 19	7000	2.00	—	—	100	100
Magnetic toner 29	Magnetic toner particle 20	5800	2.00	—	—	100	100
Magnetic toner 30	Magnetic toner particle 21	5800	2.00	—	—	100	100
Magnetic toner 31	Magnetic toner particle 22	5800	2.00	—	—	100	100
Magnetic toner 32	Magnetic toner particle 1	5800	1.80	—	—	100	100
Magnetic toner 33	Magnetic toner particle 1	5800	1.80	—	—	100	100
Magnetic toner 34	Magnetic toner particle 23	5800	2.00	—	—	100	100
Magnetic toner 35	Magnetic toner particle 24	5800	2.00	—	—	100	100
Comparative magnetic toner 1	Magnetic toner particle 1	5800	1.50	—	—	100	100
Comparative magnetic toner 2	Magnetic toner particle 17	5800	1.50	—	—	100	100
Comparative magnetic toner 3	Magnetic toner particle 1	5800	2.60	—	—	100	100
Comparative magnetic toner 4	Magnetic toner particle 1	5800	2.60	—	—	100	100
Comparative magnetic toner 5	Magnetic toner particle 1	5800	1.50	—	—	100	100
Comparative magnetic toner 6	Magnetic toner particle 1	5800	1.50	—	—	100	100
Comparative magnetic toner 7	Magnetic toner particle 15	5800	1.00	—	—	100	100
Comparative magnetic toner 8	Magnetic toner particle 15	5800	2.00	—	—	100	100
Comparative magnetic toner 9	Magnetic toner particle 16	5800	1.00	—	—	100	100
Comparative magnetic toner 10	Magnetic toner particle 16	5800	2.00	—	—	100	100
Comparative magnetic toner 11	Magnetic toner particle 1	5800	1.60	0.40	—	80	80
Comparative magnetic toner 12	Magnetic toner particle 1	5800	1.60	0.20	0.20	80	80

Magnetic toner	External addition apparatus	Operating conditions for the external addition apparatus	Operating time by the external addition apparatus	Coverage ratio A (%)	B/A (–)	Coefficient of variation on coverage ratio A (%)
Magnetic toner 25	Apparatus of FIG. 2	1.0 W/g (1800 rpm)	5 min	54.5	0.64	7.2
Magnetic toner 26	Apparatus of FIG. 2	1.0 W/g (1800 rpm)	5 min	56.6	0.74	6.5
Magnetic toner 27	Apparatus of FIG. 2	1.0 W/g (1800 rpm)	5 min	57.3	0.74	6.6
Magnetic toner 28	Apparatus of FIG. 2	1.0 W/g (1800 rpm)	5 min	54.8	0.68	6.5
Magnetic toner 29	Apparatus of FIG. 2	1.0 W/g (1800 rpm)	5 min	57.0	0.73	6.8
Magnetic toner 30	Apparatus of FIG. 2	1.0 W/g (1800 rpm)	5 min	56.6	0.75	6.8
Magnetic toner 31	Apparatus of FIG. 2	1.0 W/g (1800 rpm)	5 min	56.5	0.76	6.8
Magnetic toner 32	Apparatus of FIG. 2	1.0 W/g (1800 rpm)	5 min	51.9	0.71	6.7
Magnetic toner 33	Apparatus of FIG. 2	1.0 W/g (1800 rpm)	5 min	48.3	0.64	9.1
Magnetic toner 34	Apparatus of FIG. 2	1.0 W/g (1800 rpm)	5 min	56.4	0.71	6.6
Magnetic toner 35	Apparatus of FIG. 2	1.0 W/g (1800 rpm)	5 min	56.7	0.72	6.7
Comparative magnetic toner 1	Henschel mixer	3000 rpm	2 min	37.2	0.41	18.2
Comparative magnetic toner 2	Henschel mixer	4000 rpm	5 min	39.0	0.43	18.1
Comparative magnetic toner 3	Henschel mixer	3000 rpm	2 min	51.2	0.35	13.4
Comparative magnetic toner 4	Henschel mixer	4000 rpm	5 min	53.4	0.36	12.3
Comparative magnetic toner 5	Hybridizer	7000 rpm	8 min	43.9	0.82	13.7
Comparative magnetic toner 6	Hybridizer	7000 rpm	8 min	44.9	0.86	12.6
Comparative magnetic toner 7	Henschel mixer	4000 rpm	2 min	43.2	0.47	14.9
Comparative magnetic toner 8	Henschel mixer	4000 rpm	2 min	55.9	0.48	14.9
Comparative magnetic toner 9	Henschel mixer	4000 rpm	2 min	64.5	0.87	13.0
Comparative magnetic toner 10	Henschel mixer	4000 rpm	2 min	72.9	0.83	13.3
Comparative magnetic toner 11	Apparatus of FIG. 2	1.0 W/g (1800 rpm)	5 min	55.1	0.68	8.0
Comparative magnetic toner 12	Apparatus of FIG. 2	1.0 W/g (1800 rpm)	5 min	54.6	0.66	8.5

TABLE 4-3

Magnetic toner	Magnetic toner particle	Main peak molecular weight (Mp)	Silica fine particles (mass parts)	Titania fine particles (mass parts)	Alumina fine particles (mass parts)	Content of silica fine particles (mass %)	Content of silica fine particles in the fixed inorganic fine particles (mass %)
Comparative magnetic toner 13	Magnetic toner particle 1	5800	2.00	—	—	100	100
Comparative magnetic toner 14	Magnetic toner particle 10	3600	2.00	—	—	100	100
Comparative magnetic toner 15	Magnetic toner particle 11	8400	2.00	—	—	100	100
Comparative magnetic toner 16	Magnetic toner particle 12	5800	2.00	—	—	100	100
Comparative magnetic toner 17	Magnetic toner particle 13	5800	2.00	—	—	100	100
Comparative magnetic toner 18	Magnetic toner particle 14	5800	2.00	—	—	100	100
Comparative magnetic toner 19	Magnetic toner particle 1	5800	1.50	—	—	100	100
Comparative magnetic toner 20	Magnetic toner particle 1	5800	1.20	—	—	100	100
Comparative magnetic toner 21	Magnetic toner particle 1	5800	3.10	—	—	100	100
Comparative magnetic toner 22	Magnetic toner particle 1	5800	2.60	—	—	100	100
Comparative magnetic toner 23	Magnetic toner particle 1	5800	1.50	—	—	100	100
Comparative magnetic toner 24	Magnetic toner particle 1	5800	2.00	—	—	100	100

Magnetic toner	External addition apparatus	Operating conditions for the external addition apparatus	Operating time by the external addition apparatus	Coverage ratio A (%)	B/A (−)	Coefficient of variation on coverage ratio A (%)
Comparative magnetic toner 13	Apparatus of FIG. 2	No pre-mixing 1.0 W/g (1800 rpm)	3 min	52.6	0.62	10.6
Comparative magnetic toner 14	Apparatus of FIG. 2	1.0 W/g (1800 rpm)	5 min	54.1	0.69	6.6
Comparative magnetic toner 15	Apparatus of FIG. 2	1.0 W/g (1800 rpm)	5 min	51.2	0.58	7.1
Comparative magnetic toner 16	Apparatus of FIG. 2	1.0 W/g (1800 rpm)	5 min	55.2	0.67	6.7
Comparative magnetic toner 17	Apparatus of FIG. 2	1.0 W/g (1800 rpm)	5 min	56.7	0.69	6.7
Comparative magnetic toner 18	Apparatus of FIG. 2	1.0 W/g (1800 rpm)	5 min	53.9	0.62	7.0
Comparative magnetic toner 19	Apparatus of FIG. 2	No pre-mixing 0.6 W/g (1400 rpm)	3 min	46.7	0.48	12.5
Comparative magnetic toner 20	Apparatus of FIG. 2	No pre-mixing 0.6 W/g (1400 rpm)	3 min	43.6	0.53	13.0
Comparative magnetic toner 21	Apparatus of FIG. 2	No pre-mixing 1.6 W/g (2500 rpm)	3 min	74.0	0.54	11.5
Comparative magnetic toner 22	Apparatus of FIG. 2	No pre-mixing 0.6 W/g (1400 rpm)	3 min	69.6	0.48	11.9
Comparative magnetic toner 23	Apparatus of FIG. 2	No pre-mixing 2.2 W/g (3300 rpm)	5 min	47.6	0.88	11.8
Comparative magnetic toner 24	Apparatus of FIG. 2	1.0 W/g (1800 rpm)	5 min	37.5	0.47	13.2

Magnetic Toner Particle Production Examples 2 to 14 and 17 to 24

Magnetic toner particles 2 to 14 and 17 to 24 were obtained by following the same procedure as in Magnetic Toner Particle Production Example 1, but changing the release agent and binder resin in Magnetic Toner Particle Production Example 1 to the type and content shown in Table 3. The properties of magnetic toner particles 2 to 14 and 17 to 24 are also shown in Table 3.

An adjustment was made to raise the average circularity of the magnetic toner particle by controlling the exhaust temperature of the Turbo Mill T-250 to a somewhat high 44° C. during fine pulverization in the case of magnetic toner particle 23 and by setting to an even higher 48° C. during fine pulverization in the case of magnetic toner particle 24.

Magnetic Toner Particle Production Example 15

External addition prior to a hot wind treatment was performed by mixing 100 mass parts of magnetic toner particles 1 using an FM10C Henschel mixer (Mitsui Miike Chemical Engineering Machinery Co., Ltd.) with 0.5 mass parts of the silica fine particles used in the external addition and mixing process of Magnetic Toner Production Example 1. The external addition conditions here were a rotation rate of 3000 rpm and a processing time of 2 minutes.

Then, after being subjected to this external addition prior to a hot wind treatment, the magnetic toner particles were subjected to surface modification using a Meteorainbow (Nippon Pneumatic Mfg. Co., Ltd.), which is a device that carries out the surface modification of toner particles using a hot wind blast. The surface modification conditions were a starting material feed rate of 2 kg/hr, a hot wind flow rate of 700 L/min, and a hot wind ejection temperature of 300° C. Magnetic toner particles 15 were obtained by carrying out this hot wind treatment.

Magnetic Toner Particle Production Example 16

Magnetic toner particle 16 was obtained by following the same procedure as in Magnetic Toner Particle Production Example 15, but in this case using 1.5 mass parts for the amount of addition of the silica fine particles in the external addition prior to the hot wind treatment in Magnetic Toner Particle Production Example 15.

Magnetic Toner Production Examples 2 to 22, 27 to 32, and 34 and 35 and Comparative Magnetic Toner Production Examples 1 to 23

Magnetic toners 2 to 22, 27 to 32, and 34 and 35 and comparative magnetic toners 1 to 23 were obtained using the magnetic toner particles shown in Table 4 in Magnetic Toner

Production Example 1 in place of magnetic toner particle 1 and by performing respective external addition processing using the external addition recipes, external addition apparatuses, and external addition conditions shown in Table 4. The properties of magnetic toners 2 to 22, 27 to 32, and 34 and 35 and comparative magnetic toners 1 to 23 are shown in Table 4.

Anatase titanium oxide fine particles (BET specific surface area: 80 m^2/g, primary particle number-average particle diameter (D1): 15 nm, treated with 12 mass % isobutyltrimethoxysilane) were used for the titania fine particles referenced in Table 4 and alumina fine particles (BET specific surface area: 80 m^2/g, primary particle number-average particle diameter (D1): 17 nm, treated with 10 mass % isobutyltrimethoxysilane) were used for the alumina fine particles referenced in Table 4.

Table 4 gives the silica fine particle content (mass %) in the case where titania fine particles and/or alumina fine particles are added, in addition to silica fine particles.

For magnetic toner 15 and comparative magnetic toners 13 and 19 to 23, pre-mixing was not performed and the external addition and mixing process was carried out immediately after introduction.

The hybridizer referenced in Table 4 is the Hybridizer Model 5 (Nara Machinery Co., Ltd.), and the Henschel mixer referenced in Table 4 is the FM10C (Mitsui Miike Chemical Engineering Machinery Co., Ltd.).

Magnetic Toner Production Example 23

Magnetic toner 23 was obtained proceeding as in Magnetic Toner Production Example 1, with the exception that the silica fine particle 1 was changed to silica fine particle 2, which had been prepared by subjecting a silica with a BET specific surface area of 200 m^2/g and a primary particle number-average particle diameter (D1) of 12 nm to the same surface treatment as for silica fine particle 1. Physical properties of the magnetic toner 23 are show in Table 4. A value of 14 nm was obtained when magnetic toner 23 was submitted to magnification and observation with a scanning electron microscope and the number-average particle diameter of the primary particles of the silica fine particles on the magnetic toner surface was measured.

Magnetic Toner Production Example 24

Magnetic toner 24 was obtained proceeding as in Magnetic Toner Production Example 1, with the exception that the silica fine particle 1 was changed to silica fine particle 3, which had been prepared by subjecting a silica with a BET specific surface area of 90 m^2/g and a primary particle number-average particle diameter (D1) of 25 nm to the same surface treatment as for silica fine particle 1. Physical properties of the magnetic toner 24 are show in Table 4. A value of 28 nm was obtained when magnetic toner 24 was submitted to magnification and observation with a scanning electron microscope and the number-average particle diameter of the primary particles of the silica fine particles on the magnetic toner surface was measured.

Magnetic Toner Production Example 25

The external addition and mixing process was performed according to the following procedure using the same apparatus configuration as in Magnetic Toner Production Example 1.

As shown in Table 4, the silica fine particle 1 (2.00 mass parts) added in Magnetic Toner Production Example 1 was changed to silica fine particle 1 (1.70 mass parts) and titania fine particles (0.30 mass parts).

First, 100 mass parts of magnetic toner particles 1, 0.70 mass parts of the silica fine particles, and 0.30 mass parts of the titania fine particles were introduced and the same pre-mixing as in Magnetic Toner Production Example 1 was then performed.

In the external addition and mixing process carried out once pre-mixing was finished, processing was performed for a processing time of 2 minutes while adjusting the peripheral velocity of the outermost end of the stirring member **3** so as to provide a constant drive member **8** power of 1.0 W/g (drive member **8** rotation rate of 1800 rpm), after which the mixing process was temporarily stopped. The supplementary introduction of the remaining silica fine particles (1.00 mass part with reference to 100 mass parts of magnetic toner particle) was then performed, followed by again processing for a processing time of 3 minutes while adjusting the peripheral velocity of the outermost end of the stirring member **3** so as to provide a constant drive member **8** power of 1.0 W/g (drive member **8** rotation rate of 1800 rpm), thus providing a total external addition and mixing process time of 5 minutes.

After the external addition and mixing process, the coarse particles and so forth were removed using a circular vibrating screen as in Magnetic Toner Production Example 1 to obtain magnetic toner 25. The external addition conditions for magnetic toner 25 and the properties of magnetic toner 25 are given in Table 4.

Magnetic Toner Production Example 26

The external addition and mixing process was performed according to the following procedure using the same apparatus as in Magnetic Toner Production Example 1.

As shown in Table 4, the silica fine particle 1 (2.00 mass parts) added in Magnetic Toner Production Example 1 was changed to silica fine particle 1 (1.70 mass parts) and titania fine particles (0.30 mass parts).

First, 100 mass parts of magnetic toner particles 1 and 1.70 mass parts of the silica fine particles were introduced and the same pre-mixing as in Magnetic Toner Production Example 1 was then performed.

In the external addition and mixing process carried out once pre-mixing was finished, processing was performed for a processing time of 2 minutes while adjusting the peripheral velocity of the outermost end of the stirring member **3** so as to provide a constant drive member **8** power of 1.0 W/g (drive member **8** rotation rate of 1800 rpm), after which the mixing process was temporarily stopped. The supplementary introduction of the remaining titania fine particles (0.30 mass parts with reference to 100 mass parts of magnetic toner particle) was then performed, followed by again processing for a processing time of 3 minutes while adjusting the peripheral velocity of the outermost end of the stirring member **3** so as to provide a constant drive member **8** power of 1.0 W/g (drive member **8** rotation rate of 1800 rpm), thus providing a total external addition and mixing process time of 5 minutes.

After the external addition and mixing process, the coarse particles and so forth were removed using a circular vibrating screen as in Magnetic Toner Production Example 1 to obtain magnetic toner 26. The external addition conditions for magnetic toner 26 and the properties of magnetic toner 26 are given in Table 4.

Magnetic Toner Production Example 33

Magnetic toner 33 was obtained proceeding as in Magnetic Toner Production Example 24, with the exception that the amount of addition of silica fine particle 3 was changed from 2.00 mass parts to 1.80 mass parts. Physical properties of the

magnetic toner 33 are shown in Table 4. A value of 28 nm was obtained when magnetic toner 33 was submitted to magnification and observation with a scanning electron microscope and the number-average particle diameter of the primary particles of the silica fine particles on the magnetic toner surface was measured.

Comparative Magnetic Toner Production Example 24

A comparative magnetic toner 24 was obtained proceeding as in Magnetic Toner Production Example 1, with the exception that the silica fine particle 1 was changed to silica fine particle 4, which had been prepared by subjecting a silica with a BET specific surface area of 30 m^2/g and a primary particle number-average particle diameter (D1) of 51 nm to the same surface treatment as for silica fine particle 1. Physical properties of the comparative magnetic toner 24 are shown in Table 4. A value of 53 nm was obtained when comparative magnetic toner 24 was submitted to magnification and observation with a scanning electron microscope and the number-average particle diameter of the primary particles of the silica fine particles on the magnetic toner surface was measured.

Example 1

The Image-Forming Apparatus

The image-forming apparatus was an LBP-3100 (Canon, Inc.), which was equipped with a film fixing unit in which the fixing member in contact with the toner image was composed of a film. In addition, its fixation temperature could be varied and its printing speed had been modified from 16 sheets/minute to 20 sheets/minute. In an image-forming apparatus equipped with a small-diameter developing sleeve (diameter=10 mm), the durability was rigorously evaluated by changing the printing speed to 20 sheets/minute.

(Evaluation of the Fixing Performance)

FOX RIVER BOND PAPER (75 g/m^2) was used as the fixing media to evaluate the fixing performance, and the evaluation was carried out in a low-temperature, low-humidity environment (7.5° C., 10% RH).

The fixing performance can be rigorously evaluated by setting up conditions unfavorable to heat transfer during fixing by lowering the surrounding temperature during fixing as above in order to lower the paper temperature of the media and by setting up rubbing conditions in which the media itself is a media having a relatively large surface unevenness.

(Evaluation of the Developing Performance (Image Density and Fogging))

Using this modified apparatus and magnetic toner 1, a 3000-sheet image printing test was performed in one-sheet intermittent mode of horizontal lines at a print percentage of 2% using CS-680 (68 g/m^2) for the paper in a high-temperature, high-humidity environment (32.5° C./80% RH). After the 3000 sheets had been printed, standing was carried out for one day in a low-temperature, low-humidity environment (15° C./10% RH) and additional printing was then performed. Fogging due to defectively charged toner can be rigorously evaluated by evaluation in a low-temperature, low-humidity environment after durability testing.

According to the results, a high density was obtained before and after the durability test and an image was obtained that presented little fogging in the nonimage areas. The results of the evaluation are shown in Table 5.

The evaluation methods and associated scales used in the evaluations carried out in the examples of the present invention and comparative examples are described below.

<Durability Test Image Density>

For the image density, a solid image area was formed and the density of this solid image was measured with a MacBeth reflection densitometer (MacBeth Corporation).

The following scale was used to evaluate the reflection density of the solid image at the start of the durability test (evaluation 1).

A: very good (greater than or equal to 1.45)
B: good (less than 1.45 and greater than or equal to 1.40)
C: average (less than 1.40 and greater than or equal to 1.35)
D: poor (less than 1.35)

The following scale was used to evaluate the image density after the latter half of the durability test (evaluation 2).

Evaluation was carried out on the basis of a difference between the reflection density of the solid image at the start of the durability test and the reflection density of the solid image after the 3000-sheet durability test. Better results were gained when the difference was smaller.

A: very good (less than 0.05)
B: good (less than 0.10 and greater than or equal to 0.05)
C: average (less than 0.15 and greater than or equal to 0.10)
D: poor (greater than or equal to 0.15)

<Fogging>

A white image was output and its reflectance was measured using a REFLECTMETER MODEL TC-6DS from Tokyo Denshoku Co., Ltd. On the other hand, the reflectance was also similarly measured on the transfer paper (standard paper) prior to formation of the white image. A green filter was used as the filter. The fogging was calculated using the following formula from the reflectance before output of the white image and the reflectance after output of the white image.

Fogging(reflectance)(%)=reflectance(%) of the standard paper−reflectance(%) of the white image sample

The scale for evaluating the fogging (evaluation 3) is below.

A: very good (less than 1.2%)
B: good (less than 2.0% and greater than or equal to 1.2%)
C: average (less than 3.0% and greater than or equal to 2.0%)
D: poor (greater than or equal to 3.0%)

<Low-Temperature Fixability>

For the low-temperature fixability, images were output on FOX RIVER BOND paper at a set temperature of 200° C. while adjusting the halftone image density to provide an image density from at least 0.75 to not more than 0.80.

After this, printing was carried out with the set temperature at the fixing unit lowered in 5° C. decrements from 200° C. The fixed image was then rubbed ten times with lens-cleaning paper placed under a load of 55 g/cm^2, and the fixing lower-limit temperature was taken to be the temperature at which the decline in the density of the fixed image after rubbing exceeded 10%. A lower value for this temperature indicates a toner having a better low-temperature fixability.

The scale for scoring this evaluation (evaluation 4) is given below.

A: less than 160° C.
B: from at least 160° C. to less than 170° C.
C: from at least 170° C. to less than 180° C.
D: from at least 180° C. to less than 190° C.
E: from at least 190° C. to less than 200° C.

Examples 2 to 35 and Comparative Examples 1 to 24

Toner evaluations were carried out under the same conditions as in Example 1 using magnetic toners 2 to 35 and comparative magnetic toners 1 to 24 for the magnetic toner. The results of the evaluations are shown in Table 5.

TABLE 5-1

		Evaluation 1 (Starting density)	Evaluation 2 (Extent of density decline)	Evaluation 3 (Fogging)	Evaluation 4 (Low temperature fixability)
Magnetic toner 1	Magnetic toner particle 1	A(1.50)	A(0.04)	A(0.6)	A(150)
Magnetic toner 2	Magnetic toner particle 1	A(1.49)	B(0.08)	A(0.5)	A(150)
Magnetic toner 3	Magnetic toner particle 1	A(1.49)	B(0.07)	B(0.9)	A(150)
Magnetic toner 4	Magnetic toner particle 1	A(1.47)	B(0.09)	B(1.3)	A(155)
Magnetic toner 5	Magnetic toner particle 1	B(1.44)	B(0.06)	A(1.1)	A(155)
Magnetic toner 6	Magnetic toner particle 1	B(1.44)	B(0.07)	B(1.3)	A(155)
Magnetic toner 7	Magnetic toner particle 1	A(1.47)	A(0.04)	A(0.8)	B(160)
Magnetic toner 8	Magnetic toner particle 1	A(1.46)	B(0.07)	A(1.0)	B(160)
Magnetic toner 9	Magnetic toner particle 1	A(1.46)	B(0.08)	B(1.3)	B(160)
Magnetic toner 10	Magnetic toner particle 1	A(1.45)	B(0.06)	B(1.6)	A(155)
Magnetic toner 11	Magnetic toner particle 1	B(1.43)	B(0.05)	B(1.8)	A(155)
Magnetic toner 12	Magnetic toner particle 1	A(1.48)	B(0.05)	A(1.1)	B(165)
Magnetic toner 13	Magnetic toner particle 1	A(1.48)	B(0.07)	B(1.3)	B(165)
Magnetic toner 14	Magnetic toner particle 2	A(1.47)	A(0.04)	A(0.7)	A(155)
Magnetic toner 15	Magnetic toner particle 1	A(1.48)	B(0.05)	B(1.2)	B(160)
Magnetic toner 16	Magnetic toner particle 3	A(1.47)	B(0.09)	A(1.1)	A(150)
Magnetic toner 17	Magnetic toner particle 4	A(1.47)	A(0.03)	A(1.0)	B(160)
Magnetic toner 18	Magnetic toner particle 5	A(1.49)	A(0.04)	A(0.8)	A(155)
Magnetic toner 19	Magnetic toner particle 6	A(1.48)	A(0.04)	A(0.8)	A(150)
Magnetic toner 20	Magnetic toner particle 7	A(1.46)	A(0.04)	A(0.8)	A(150)
Magnetic toner 21	Magnetic toner particle 8	A(1.47)	C(0.12)	A(0.7)	A(150)
Magnetic toner 22	Magnetic toner particle 9	A(1.47)	A(0.04)	A(0.9)	C(170)
Magnetic toner 23	Magnetic toner particle 1	A(1.50)	A(0.04)	A(0.6)	A(155)
Magnetic toner 24	Magnetic toner particle 1	A(1.47)	A(0.04)	A(1.0)	A(150)
Magnetic toner 25	Magnetic toner particle 1	A(1.49)	B(0.09)	A(1.0)	A(150)
Magnetic toner 26	Magnetic toner particle 1	A(1.49)	B(0.05)	A(0.4)	A(150)
Magnetic toner 27	Magnetic toner particle 18	A(1.48)	B(0.06)	A(0.6)	A(150)
Magnetic toner 28	Magnetic toner particle 19	A(1.49)	A(0.04)	A(0.9)	A(150)
Magnetic toner 29	Magnetic toner particle 20	A(1.48)	A(0.04)	A(0.8)	A(150)
Magnetic toner 30	Magnetic toner particle 21	A(1.48)	B(0.06)	A(0.9)	A(155)
Magnetic toner 31	Magnetic toner particle 22	A(1.45)	B(0.08)	A(1.1)	B(160)
Magnetic toner 32	Magnetic toner particle 1	A(1.48)	B(0.05)	A(1.1)	A(150)
Magnetic toner 33	Magnetic toner particle 1	A(1.47)	B(0.07)	B(1.5)	A(150)
Magnetic toner 34	Magnetic toner particle 23	A(1.48)	B(0.07)	A(1.0)	A(150)
Magnetic toner 35	Magnetic toner particle 24	A(1.49)	B(0.06)	B(1.2)	A(150)

TABLE 5-2

		Evaluation 1 (Starting density)	Evaluation 2 (Extent of density decline)	Evaluation 3 (Fogging)	Evaluation 4 (Low temperature fixability)
Comparative magnetic toner 1	Magnetic toner particle 1	D(1.31)	C(0.13)	B(1.6)	D(185)
Comparative magnetic toner 2	Magnetic toner particle 17	D(1.22)	D(0.18)	B(1.4)	D(185)
Comparative magnetic toner 3	Magnetic toner particle 1	C(1.37)	B(0.09)	C(2.4)	D(185)
Comparative magnetic toner 4	Magnetic toner particle 1	C(1.36)	B(0.08)	C(2.1)	D(185)
Comparative magnetic toner 5	Magnetic toner particle 1	C(1.36)	C(0.14)	B(1.2)	D(180)
Comparative magnetic toner 6	Magnetic toner particle 1	C(1.39)	D(0.16)	A(1.1)	D(180)
Comparative magnetic toner 7	Magnetic toner particle 15	C(1.35)	C(0.12)	B(1.8)	D(180)
Comparative magnetic toner 8	Magnetic toner particle 15	C(1.35)	B(0.09)	B(1.6)	D(185)
Comparative magnetic toner 9	Magnetic toner particle 16	B(1.41)	C(0.13)	B(1.4)	D(185)
Comparative magnetic toner 10	Magnetic toner particle 16	B(1.42)	D(0.16)	C(2.0)	E(190)
Comparative magnetic toner 11	Magnetic toner particle 1	C(1.39)	C(0.13)	B(1.5)	D(180)
Comparative magnetic toner 12	Magnetic toner particle 1	C(1.38)	C(0.13)	B(1.7)	D(180)
Comparative magnetic toner 13	Magnetic toner particle 1	B(1.44)	B(0.08)	D(3.6)	C(175)
Comparative magnetic toner 14	Magnetic toner particle 10	B(1.43)	C(0.14)	D(3.1)	C(175)
Comparative magnetic toner 15	Magnetic toner particle 11	B(1.44)	C(0.10)	C(2.3)	E(190)
Comparative magnetic toner 16	Magnetic toner particle 12	A(1.45)	C(0.10)	A(1.1)	D(180)
Comparative magnetic toner 17	Magnetic toner particle 13	B(1.44)	C(0.10)	B(1.9)	D(180)
Comparative magnetic toner 18	Magnetic toner particle 14	B(1.44)	B(0.08)	C(2.1)	E(195)
Comparative magnetic toner 19	Magnetic toner particle 1	C(1.36)	B(0.09)	D(3.2)	D(180)
Comparative magnetic toner 20	Magnetic toner particle 1	B(1.40)	C(0.12)	C(2.3)	D(180)
Comparative magnetic toner 21	Magnetic toner particle 1	C(1.37)	D(0.15)	B(1.9)	E(190)
Comparative magnetic toner 22	Magnetic toner particle 1	B(1.40)	B(0.09)	D(3.3)	E(190)
Comparative magnetic toner 23	Magnetic toner particle 1	B(1.43)	C(0.12)	C(2.2)	D(180)
Comparative magnetic toner 24	Magnetic toner particle 1	D(1.34)	C(0.12)	C(2.8)	D(185)

While the present invention has been described with reference to exemplary embodiments, it is to be understood that the invention is not limited to the disclosed exemplary embodiments. The scope of the following claims is to be accorded the broadest interpretation so as to encompass all such modifications and equivalent structures and functions.

This application claims the benefit of Japanese Patent Application No. 2011-285912, filed on Dec. 27, 2011, which is hereby incorporated by reference herein in its entirety.

REFERENCE SIGNS LIST

1: main casing
2: rotating member
3, **3***a*, **3***b*: stirring member
4: jacket
5: raw material inlet port
6: product discharge port
7: center shaft
8: drive member
9: processing space
10: end surface of the rotating member
11: direction of rotation
12: back direction
13: forward direction
16: raw material inlet port inner piece
17: product discharge port inner piece
d: distance showing the overlapping portion of the stirring members
D: stirring member width
100: electrostatic latent image-bearing member (photosensitive member)
102: toner-carrying member
103: developing blade
114: transfer member (transfer charging roller)
116: cleaner container
117: charging member (charging roller)
121: laser generator (latent image-forming means, photoexposure apparatus)
123: laser
124: pick-up roller
125: transport belt
126: fixing unit
140: developing device
141: stirring member

The invention claimed is:

1. A magnetic toner comprising
magnetic toner particles containing a binder resin, a release agent, and a magnetic body, and
inorganic fine particles present on the surface of the magnetic toner particles,
wherein;
the inorganic fine particles present on the surface of the magnetic toner particles comprise metal oxide fine particles,
the metal oxide fine particles containing silica fine particles, and optionally containing titania fine particles and alumina fine particles, and a content of the silica fine particles being at least 85 mass % with respect to a total mass of the silica fine particles, the titania fine particles and the alumina fine particles,
wherein;
when a coverage ratio A(%) is a coverage ratio of the magnetic toner particles' surface by the inorganic fine particles and a coverage ratio B(%) is a coverage ratio of the magnetic toner particles' surface by the inorganic fine particles that are fixed on the magnetic toner particles' surface,
the magnetic toner has a coverage ratio A of at least 45.0% and not more than 70.0% and a coefficient of variation on the coverage ratio A of not more that 10.0%, and
a ratio [coverage ratio B/coverage ratio A] of the coverage ratio B to the coverage ratio A of at least 0.50 and not more than 0.85,
wherein
the binder resin comprises a styrene resin and, in a measurement using gel permeation chromatography of a tetrahydrofuran-soluble matter in the magnetic toner, a peak molecular weight (Mp) of a main peak is from at least 4000 to not more than 8000,
and wherein
the release agent comprises at least one of fatty acid ester compounds selected from the group consisting of a tetrafunctional fatty acid ester compound, a pentafunctional fatty acid ester compound and a hexafunctional fatty acid ester compound, and the fatty acid ester compound has a melting point of from at least 60° C. to not more than 90° C.

2. The magnetic toner according to claim **1**, wherein the fatty acid ester compound comprises an ester compound of a fatty acid having from at least 18 to not more than 22 carbon atoms and an alcohol having from at least 4 to not more than 6 hydroxyl groups.

* * * * *